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menon is evidently connected with their colloidal nature, and may well, in a greater or less degree, be common to all colloidal solutions.

If the rises are regarded as due solely to osmotic pressure proper, the anomalous relations between osmotic rise and concentration can only be set down to variations in the mean size of the molecule. The effects of co-volume and of intermolecular attraction cannot, at such low concentrations, account for $c-H$ curves so strongly curved as those of tables I and IV. There must, then, in a given viscoid solution of caoutchouc be a predominance of large, highly associated molecules at lowest concentrations, and a rapidly increasing dissociation as the concentration rises. Also, in a solution of given concentration, molecular association must increase as the viscosity decreases. These conclusions, however, are directly opposed to what is known of the general relations existing between concentration, molecular association, and viscosity.

A more probable explanation would seem to lie in the colloidal characteristics of caoutchouc and the two-phase constitution of its solutions. There can hardly be any doubt that solutions of caoutchouc, like those of gelatin (see Garrett, *Phil. Mag.*, 1903, [vi], 6, 374), are composed of a sol-phase and a gel-phase, the latter of which, although uniformly dispersed in the former, has sufficient cohesion of its own to impart a certain elasticity to the solution. The ropy habit of moderately dilute caoutchouc solutions affords prima facie evidence of a gel-phase. This hypothesis, then, supposes that caoutchouc solutions of near 100 per cent. consist of little sol and much mechanically strong gel containing but little solvent; that very dilute solutions consist of relatively more sol and relatively little gel, the latter weak and highly distended; and that between the extremes there is a continuous gradation. Hence the viscosity, as measured by efflux, rises much more rapidly than the total concentration. At any given concentration there is a metastable equilibrium between the gel-phase and the sol-phase, the swelling tendencies of the former being counteracted by the true osmotic pressure of the latter. Spontaneous or accelerated ageing tends to shift the equilibrium in favour of the sol-phase.

Supposing, then, that a caoutchouc solution has part of its volume occupied by sol and the remainder by gel, the observed osmotic rises may be accounted for in two ways. Either, firstly, the gel-phase is osmotically inoperative, and the rise depends solely on the concentration of the sol-phase. If that were so, it would follow that as the total concentration rises the sol-phase becomes more concentrated than the gel-phase, and that as the viscosity of a given solution decreases the sol-phase becomes more dilute. Or, secondly, so much of the gel-phase as is in contact with the

diaphragm (corresponding with the ratio of gel-volume to sol-volume in the liquid) exerts simultaneously a pressure of the same character as that which causes caoutchouc, gelatin, etc., to swell when immersed in solvents, the observed rise being then a composite one. One would then expect the pressure developed inside a semi-permeable diaphragm to reach many atmospheres as the solution approached 100 per cent.; and, indeed, the pressures capable of being exerted by swelling colloids are well known to be of no mean magnitude. Which alternative is the more probable is not easy to decide in the present state of knowledge.

To the question of the molecular weight of dissolved caoutchouc the osmotic rises give no very definite answer. The van't Hoff relation can be applied only to the sol-phase, and postulates that the concentration of that phase be known; but with the dilutest solutions, in which the gel-phase may be assumed to have almost disappeared, the measurement of osmotic pressure becomes very uncertain. From the data in tables I—V, a convergence of the molecular-weight value towards 100,000 is indicated in benzene and light petroleum solutions. The molecular weight of gutta-percha in benzene solution appears to be considerably smaller, since 40,000 is the limit towards which the values shown in table VII converge.

UNIVERSITY COLLEGE,
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CXCVIII.—*The Velocities of Flame in Mixtures of Methane and Air.*

By ALBERT PARKER and ALAN VICTOR RHEAD.

THE progress of flame in mixtures of methane and air and hydrogen and air in various proportions was carefully investigated by Mallard and Le Chatelier (*Bull. Soc. chim.*, 1882, [ii], 39, 369). They devised several methods of measuring velocities of flame, but none of these was entirely satisfactory. In the case of mixtures with methane, the velocities were determined by passing the gases through a tube at a known rate, igniting the mixture at the end, and gradually reducing the velocity until a point was reached, when the flame commenced to travel back along the tube. At this point the velocity of inflammation must have been greater than the rate of flow of the gas. The velocity of flame was taken as the minimum speed at which the gas had to be driven to prevent the

mixture firing back. Bunte (*Ber.*, 1898, **31**, 19) also used a similar method in his experiments on the initial velocities of hydrogen, coal gas, acetylene, and methane when mixed with air. The results of the above-mentioned investigators are of great value in connexion with the combustion of air-gas mixtures for heating or lighting purposes, but for the study of fire-damp explosions in coal mines it is necessary to make observations of the properties of flame as it "travels through" mixtures of methane and air.

The object of the following experiments was to measure the velocities of the flame of mixtures of methane and air at different points in a tube. At the same time it was decided to investigate the effect of material by using tubes of copper, lead, iron, and glass.

Preparation of the Gaseous Mixtures.—The gases were mixed over water in a graduated gas-holder of 150 litres' capacity. About 100 litres of each mixture was made, and this was sufficient to allow each experiment to be carried out several times if necessary. A careful analysis of each mixture was made by explosion, after the addition of measured quantities of pure methane and oxygen to ensure complete combustion.

Methane.—This gas was prepared by Campbell and Parker's method (*T.*, 1913, **103**, 1292) from aluminium carbide and water; it was purified as described by these authors.

Apparatus.—In the first experiments carried out, the tubes used were each approximately 2.5 cm. in diameter and 10 metres long, and were made up of shorter lengths held close together by stout rubber bands. In the tubes of lead, copper, and iron, short glass tubes (5 cm. long and 2.5 cm. wide) were interposed at every metre, to act as windows for observing the flame. It was found, however, that accurate results could not be obtained by this method, as usually the flame travelled at too great a velocity to be easily followed by the eye.

This method was therefore abandoned, and the following, which afterwards proved to be most efficient, was adopted.

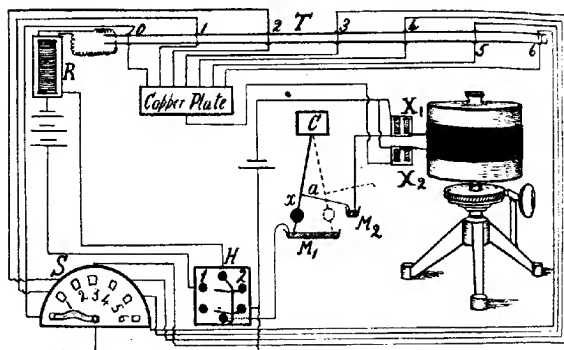
The arrangement of the recording apparatus is shown in Fig. 1. Instead of following the progress of the explosion by eye, as in the earlier experiments, thin strips of Wood's alloy * (melting at 72°) are used as flame indicators. These are stretched across the middle of the tube *T* at the points of connexion (0, 1, 2, 3, 4, 5, and 6) of the shorter lengths. The metal bridges are then placed in electrical connexion with the magnet *X*, by means of the switchboard *S* and a copper plate. The firing agent employed consists of a

* The metal strips are made by pouring the molten alloy down the channel produced by folding a piece of paper at an angle of 60°. The streak of metal must not be disturbed while cooling, otherwise it becomes brittle.

single-break spark produced from the Ruhmkorff coil (R), by screwing up the hammer break of the primary coil, and rapidly breaking the circuit by moving the mercury switch H from position 1 to 2. As soon as the flame reaches O , the metal bridge at this point is melted, releasing the stylus X_2 , and producing an upward mark on the moving drum. The switch S is then rapidly moved to position 1, again completing the magnet circuit until the corresponding bridge is melted, and so on until all the bridges have been broken.

The velocity of the revolving drum is measured by means of a clock pendulum. When the pendulum is in the position (x), the electro-magnet X_1 is in connexion with an accumulator, by way of the mercury contained in M_1 and M_2 , the copper wire (a) and the

FIG. 1.



mercury switch H . When the pendulum is in any other position the connexion is broken, since the wire (a) is raised above the surface of the mercury in M_2 . In this way the stylus X is moved up and down with each swing, and corresponding lines are traced on the blackened paper. From the time of one swing of the pendulum, the distances between the bridges, and the distances between the styli marks on the drum, the velocity of an explosion may be calculated.



Results of Experiments.

(i) *Curved Tubes.*—In all cases the mixtures were fired near an open end of the tube, the further end being closed. In the first experiments carried out, in which the Wood's alloy bridges were

used as flame indicators, the explosions were examined in tubes of glass, copper, iron, and lead, each approximately 10 metres long and 2.5 cm. in diameter. These 10-metre tubes consisted of a horizontal 5-metre length placed vertically above a 4-metre length, the two being joined by a 1-metre semi-circular tube. The two horizontal portions were made up of shorter pieces, with bridges between, and held close together by stout rubber bands; the glass windows, previously interposed in the metal tubes, were removed. In some experiments the mixtures were fired from the upper ends of the tubes, and others from the lower ends. Mixtures of methane and air containing 6.9, 7.3, 7.75, and 8.4 per cent. of methane were examined.

It was found that the bends in the tubes had some effect on the results. When fired from the upper end, the velocities of the 6.9 and 7.3 per cent. mixtures were generally found to decrease as the flame descended the bend, whereas when fired from the lower end the velocities increased as the flame ascended. The following results obtained in the iron tube of 2.72 cm. diameter, with a 7.3 per cent. mixture, serve as an example.

Methane = 7.3; air = 92.7 per cent.

Bridges numbered from firing point.	Distance in cm.	Velocity of explosion in cm. per second. Direction of flame.	
			
0-1	106	36.4	37.0
1-2	100	35.4	35.5
2-3	100	37.8	39.0
3-4	100	46.6	43.3
4-5	100	46.6	73.9
5-6	100	37.5	42.2
6-7	100	47.5	41.0
7-8	100	37.9	47.5
8-9	100	38.0	36.4
9-10	100	41.6	42.6

In the above results it is noticeable that the velocity decreased from 46.6 to 37.5 cm. per second as the flame descended the bend, whereas the velocity increased from 43.3 to 73.9 cm. per second as the flame ascended.

When the richer mixtures were sparked, it was found that the propagation of combustion always increased considerably at the bend, whether the flame were made to ascend or descend. Probably the effect of the bend was similar to that produced on firing a mixture from the closed end of a tube.

This is illustrated by the following results, taken from those obtained with a 7.75 per cent. mixture in the iron tube.

Methane=7.75; air=92.25 per cent.

Bridges numbered from firing point.	Distance in cm.	Velocity of explosion in cm. per second. Direction of flame.	
		↶	↷
0—1	107	40.3	40.0
1—2	100	36.0	36.5
2—3	100	48.2	41.8
3—4	100	44.7	49.3
4—5	100	42.6	76.5
5—6	100	86.2	94.5
6—7	100	44.7	56.9
7—8	100	41.1	41.2
8—9	100	41.1	40.7
9—10	100	45.9	45.9

From the above results it is noticeable that the velocity increased from 42.6 to 86.2 cm. per second as the flame descended the bend, and from 49.3 to 94.5 cm. per second as the flame ascended.

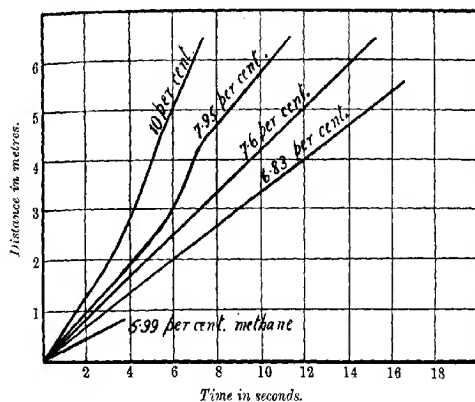
(ii) *Straight Tubes*.—As the effect of a bend in the explosion tube, on the velocities of flame, varied considerably with the composition of the gaseous mixture, the curved 10-metre tubes were replaced by straight horizontal tubes, each about 6.5 metres long. It had also been found extremely difficult to make air-tight joints with rubber bands; these were therefore removed, and the joints made with soft wax. The tubes were always tested before use, by exhaustion. The gases were fired, as in previous experiments, near an open end of the tube, the further end being closed. Mixtures of methane and air varying in composition from the lower to the upper limits have been examined.

Curves plotted from the results obtained in the glass tubes of 2.65 cm. internal diameter, with mixtures containing different proportions of methane, are shown in Figs. 2 and 3. The ordinates represent the distances travelled by the flame, and the abscissae represent the times in seconds. On sparking the 5.99 and 12.25 per cent. mixtures, the explosion travelled far enough to melt the first two bridges, but died out before reaching the third. The same thing occurred when these mixtures were fired in the tubes of copper, iron, or lead. The propagation of flame in mixtures containing 6.83 and 7.6 per cent. of methane took place with a fairly uniform velocity throughout the entire length of 6.5 metres; similar results were obtained in the metal tubes.

When 11.74 per cent. was sparked, it was generally found that the propagation of flame took place with a uniform velocity; but sometimes, even in the same tube, the velocity increased from about 38 cm. per second at the fifth metre to 50 or 60 cm. per second at the sixth. In one experiment in the iron tube the rate

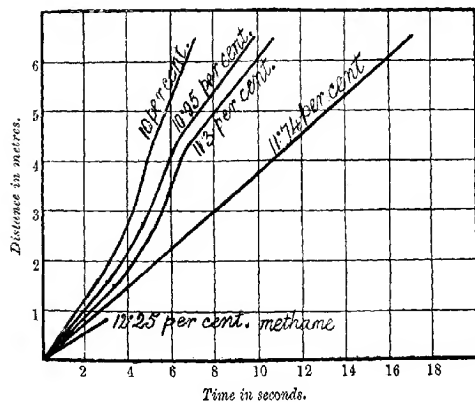
of propagation rose to 101.5 cm. per second in the second metre, afterwards falling to a fairly uniform velocity of 38 cm. per second

FIG. 2.



until the sixth metre was reached, when a slight acceleration again occurred.

FIG. 3.



In the other mixtures examined, containing 7.95, 10, 10.95, and 11.3 per cent. of methane, the explosion always travelled in a manner similar to that given in the curves. The velocity of the

flame was perfectly uniform in the first metre, and when the experiments were repeated, constant results were obtained for the same tube. In the second and third metres, the flame began to oscillate, but not always to the same extent, even when the experiments were repeated under apparently the same conditions. At the fourth and fifth metres the rate of propagation suddenly increased, and the velocity measurements in this portion of the tube varied by as much as 25 per cent. in different experiments. At the sixth metre the flame slowed down to a fairly uniform velocity.

In some experiments with the less explosive mixtures it was noticed that immediately after the setting up of vibratory movements the flame was extinguished. This was probably due to the violent agitation, causing the mixing of the burning gases with a large quantity of burnt mixture.

From the above results it may be concluded that the propagation of flame in mixtures of methane and air generally occurs in three distinct periods when fired in a tube from an open to a closed end. The flame first travels with a perfectly uniform velocity; vibratory movements are then set up, and immediately afterwards the rate of explosion suddenly increases. In the third period the velocity again falls to a fairly uniform rate as the flame approaches the closed end of the tube.

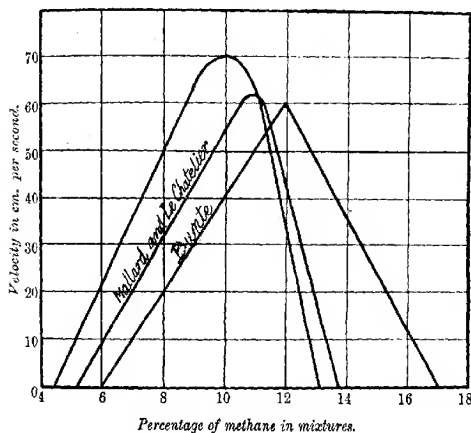
(iii) *Initial Period of Explosion.*—From the above experiments it has been found that the measurements of velocity in the second or vibratory period of explosion varied considerably. Values of the times required for the combustion of the mixtures throughout the entire 6.5 metres could not therefore be obtained sufficiently constant to enable the effect of the material of the tube to be determined. The only results that may be used for this purpose are those which were obtained in the first period, as this is the only period in which perfectly constant and uniform measurements of velocity could be made. The rates of propagation of flame are given in the following table. The internal diameters of the tubes were: glass, 2.65 cm.; lead, 2.64 cm.; copper, 2.3 cm.; and iron, 2.72 cm.:

Methane in mixtures. Per cent.	Initial velocities in cm. per second.			
	Glass.	Lead.	Copper.	Iron.
5.99	21.72	19.42	18.32	21.22
6.83	33.4	32.52	32.68	34.1
7.6	45.6	43.5	42.4	43.8
7.95	48.6	48.2	45.2	—
8.94	63.66	58.7	59.4	63.3
10.0	69.8	65.0	63.2	67.3
10.98	61.1	53.9	54.1	57.5
11.3	53.3	45.4	47.7	50.6
11.74	36.9	35.2	34.5	36.1

The velocities measured in the lead tube are lower than those in the glass. The diameters of the two tubes are so very nearly the same that the differences observed in the velocities must have been due to the effect of material.

Lead, being a far better conductor of heat than glass, must have cooled the burning gases, and so reduced the speed of propagation of the flame. The values obtained in copper are generally lower than those in lead; this may be accounted for by the better conductivity for heat and the smaller diameter of the copper tube. In the iron tube the velocities of the flame were found to be greater than in the lead (due probably to the larger diameter), but less than in

FIG. 4.



glass. From these results it may therefore be concluded that the initial velocities of flame in mixtures of methane and air, in tubes of the same diameter, vary with the heat-conductivity of the material of the tube; the greater the conductivity for heat, the smaller the velocity of the flame.

The initial velocities measured in the glass tube are shown graphically in Fig. 4, where the rates of inflammation are plotted against the amount of methane contained in the mixtures. The curve has been produced to the line of zero velocity, where the points of intersection should approximately represent the lower and upper limits of explosion of methane and air. This velocity curve appears to give the lower and upper limit values as 4.5 and 13.1 per

cent. respectively. Direct determinations of the limits place the lower value at 5.77 per cent. (Parker, this vol., p. 1002), and the upper value at 12.8 per cent. (Eitner, *J. für Gasbeleuchtung*, 1902, 45). The most explosive mixture, if considered to be the one of maximum velocity, contains about 10 per cent. of methane, and travels at an initial rate of 70 cm. per second.

Curves of the results of Mallard and Le Chatelier and of Bunte, who used the method of igniting the mixtures at the end of a tube, are also shown in the same diagram. The lower velocities and higher methane percentages obtained by these investigators are probably to be explained by the different method of determination and by the fact that the methane they used could not have been very pure.

General Conclusions.

(1) The propagation of flame in mixtures of methane and air generally occurs in three distinct periods when fired from an open to a closed end of a tube. In the first period the flame travels with a constant and uniform velocity.

The second period consists of vibratory movements and a sudden increase in velocity. In the third period the rate again falls to a uniform value, as the flame approaches the closed end of the tube.

(2) In tubes of a given diameter the initial velocity of explosion varies with the material of the tube; the velocity is less in tubes possessing a high conductivity for heat.

(3) The maximum initial velocity is possessed by a mixture containing 10 per cent. of methane, the rate of propagation of which is 70 cm. per second. The initial velocity then falls with change of methane content, moving towards zero at 4.5 and 13.1 per cent.

(4) The effect of a bend in the explosion tube varies considerably with the nature of the bend and the percentage composition of the mixture.

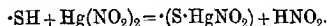
It is intended to investigate further the conditions affecting the explosion of methane with air.

THE UNIVERSITY,
MANCHESTER.

CXCI_X.—*Action of Monochloroacetic Acid on Thiocarbamide and Monoalkylated Thiocarbamides.*

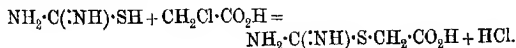
By PRAFULLA CHANDRA RÂY and FRANCIS VITO FERNANDES.

ONE of us (P., 1914, **30**, 140) has shown that whenever mercuric nitrite is treated with thiocarbamide or any other thio-compound which admits of the possibility of furnishing the thiol group (SH) by tautomeric changes, the primary reaction is of the type



It seemed to us that clearer light would be thrown on the mechanism of tautomeric changes by studying the reaction of thiocarbamide—a typical representative of this class of substances—and also its substituted alkyl derivatives with monochloroacetic acid. The expectation has been fully realised.

Volhard found that by the interaction of thiocarbamide and monochloroacetic acid, glycolylthiocarbamide was formed (*Annalen*, 1873, **166**, 385). This substance is now regarded as ψ - or *iso*-thiohydantoin, and it is now generally admitted that during its formation the parent substance, thiocarbamide, assumes the static configuration of iminothiocarbamic acid (compare Dixon and Taylor, T., 1912, **101**, 2502). As Volhard brought about the reaction by gentle heating, hydrogen chloride and water were simultaneously eliminated, resulting in the formation of the above cyclic compound. In the present paper it will be shown that by the interaction of the components in aqueous solution in the cold, condensation of the simple character represented by the following equation takes place:

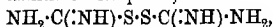


If, however, the components are brought together in acetone solution in the cold, condensation of exactly the same type occurs, with this difference, that the hydrogen chloride which is eliminated is fixed by the base, with the formation of its hydrochloride. Glycine itself has feebly basic properties, and forms a hydrochloride; the present compound is evidently a stronger base, as it contains an amidine group. Monomethyl- and monoallyl-thiocarbamides also give rise to the corresponding condensation products in acetone solution, but no condensation takes place in aqueous solution. No sharp melting point of any of these compounds could be determined, as they all decompose, with slight charring, at about 200°. On examining the results of analysis, it

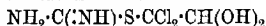
will be noticed that the purest products were obtained from the alkylated thiocarbamides.

The formation of these compounds throws some light on the constitution and reactions of thiocarbamides. Dixon and Taylor (*loc. cit.*) state that in the formation of isothiohydantoin "the parent thiocarbamide has behaved as a thiourea," but they add that a compound of the type $\text{H}_2\text{N}\cdot\text{C}(\text{NH})\cdot\text{SX}$ "is essentially unstable, and there does not appear to be any reason why conjugation with a molecule of haloid acid should render it stable." They are further of the opinion that "mere dissolution in the cold by a non-hydrolysing solvent has no effect in producing hydrogen chloride; but this is eliminated in presence of various hydrolysts." The successful isolation of the hydrochlorides described in this paper, and that in a non-ionising solvent like acetone, disposes of this hypothesis.

Moreover, Werner has shown (T., 1912, 101, 2166) that in the formation of formamidine disulphide,



by the interaction of iodine and thiocarbamide, a tautomeric change of the latter is involved; the halogen acid which is eliminated combines with the base, resulting in the formation of its hydriodide. It is evident that not only free halogen, but also a halogenated compound, which can readily part with its halogen, is equally effective in this respect. Another instance of the tautomerism of thiocarbamide is the formation of the compound



recently isolated by Sen (*Proc. Asiatic Soc. Bengal*, 1914) by the interaction of thiocarbamide and chloral hydrate (compare Coppin and Titherley, this vol., p. 32).

EXPERIMENTAL.

Formamidine-thiolacetic Acid, $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$.

The components, dissolved separately in water, were mixed and allowed to remain overnight. A white, amorphous product was obtained, which was well washed with cold water and dried in a vacuum. The substance was sparingly soluble in hot water:

0.1849 gave 0.1831 CO_2 and 0.0747 H_2O . $\text{C}=27.00$; $\text{H}=4.59$.

0.0707 „ 12.8 c.c. N_2 at 34.5° and 760 mm. $\text{N}=19.64$.

0.1318 „ 0.2157 BaSO_4 . $\text{S}=22.47$.

$\text{C}_3\text{H}_6\text{O}_2\text{N}_2\text{S}$ requires $\text{C}=26.86$; $\text{H}=4.47$; $\text{N}=20.89$; $\text{S}=23.89$ per cent.

The slightly lower percentages of nitrogen and sulphur point to the fact that the compound was not obtained quite pure. Unlike

the compounds from the substituted thiocarbamides, it had a slight tendency to decompose.

The *hydrochloride* was obtained as a white, crystalline substance when the components were mixed in acetone solution as before and left for twenty-four hours. It was freely soluble in hot water, and moderately so in hot alcohol:

0.1551 gave 0.1248 AgCl and 0.2264 BaSO₄. Cl=19.90; S=20.04.

C₃H₅O₂N₂S.HCl requires Cl=20.80; S=18.77 per cent.

As the analysis indicates, this hydrochloride was also obtained in a somewhat impure state.

Methylformamidinethiolacetic Acid Hydrochloride,
NHMe·C(NH)·S·CH₂·CO₂H.HCl.

The solvent used was acetone, as in the previous instance. Long, white needles were obtained, which were readily soluble in water:

0.0883 gave 0.0720 AgCl. Cl=20.16.

0.1406 „ 0.1802 BaSO₄. S=17.59.

0.0587 „ 8.2 c.c. N₂ at 31° and 760 mm. N=15.24.

C₃H₅O₂N₂S.HCl requires Cl=19.24; S=17.34; N=15.17 per cent.

The chlorine of this compound could also be estimated by directly precipitating it as silver chloride in aqueous solution by means of silver nitrate. The substance is therefore a true hydrochloride.

Allylformamidinethiolacetic Acid Hydrochloride,
C₃H₅·NH·C(NH)·S·CH₂·CO₂H.HCl.

In this case, clusters of thin, white needles were obtained, which were soluble in water:

0.0608 gave 0.0744 CO₂ and 0.0346 H₂O. C=33.44; H=6.32.

0.092 „ 11.8 c.c. N₂ at 31° and 760 mm. N=14.12.

0.0718 „ 0.0518 AgCl. Cl=17.84.

0.0823 „ 0.0932 BaSO₄. S=15.55.

C₆H₁₀O₂N₂S.HCl requires C=34.20; H=5.22; N=13.30;
Cl=16.86; S=15.20 per cent.

PRESIDENCY COLLEGE,
CALCUTTA.

CC.—*Magnesium Boride and Amorphous Boron.*

By RAMES CHANDRA RAY.

THE object of the present investigation was to determine whether, as Winckler (*Ber.*, 1890, **23**, 772) and Moissan (*Compt. rend.*, 1892, **114**, 392) have suggested, there might exist borides of magnesium other than the boride Mg_3B_2 . Preliminary experiments were carried out in which boron trioxide and magnesium powder were heated in varying proportions, and to different temperatures. However, so far as could be ascertained from the analyses of the products, and from the action of water and acid on them, no other boride could be obtained by this method. When a mixture of 1 part of boron trioxide was heated with $2\frac{1}{2}$ parts of magnesium powder to a red heat in a current of hydrogen for forty-five minutes, a product was obtained which was almost completely soluble in dilute hydrochloric acid, and appeared, from the results of analyses, to consist of magnesium boride, Mg_3B_2 , and magnesium oxide in the theoretical proportions. If this product was heated to a higher temperature, or for a long time at a red heat, magnesium was driven off, and a mixture of amorphous and crystalline boron separated. Free boron was always obtained if excess of boron trioxide was used, and if excess of magnesium was employed, the product had a metallic appearance, and seemed to contain free magnesium.

After completing these preliminary experiments the preparation of magnesium boride from magnesium and boron was attempted, and as it was found that crystalline boron and magnesium did not enter into combination, when they were heated together, the experiments were carried out with amorphous boron. The magnesium and boron were heated together in an iron vessel, which was lined with a mixture of magnesia with a little boric acid. The vessel was fitted with a screw cap, and a rapid stream of hydrogen was passed through it from the commencement of the experiment until the apparatus had become quite cold. The vessel was heated to a bright red heat.

On analysing the product of the reaction, it was found that it always contained from 8 to 9 per cent. of oxygen, and as the only possible source of this oxygen was the substance which was supposed to be amorphous boron, it was necessary to carry out a series of experiments to determine whether this was actually the case.

Moissan (*loc. cit.*), who described a method of preparing amorphous boron by the reduction of boron trioxide with mag-

nesium powder, stated that the product contained as much as 95 per cent. of boron. In 1909 Weintraub (*Trans. Amer. Electrochem. Soc.*, **16**, 165) carried out an investigation on the same subject, but as this journal was not available in Bangalore, and as the paper was not abstracted into other journals, I was not acquainted with the results of his experiments until after the completion of my own work. He found that the so-called amorphous boron always contained oxygen, and drew the conclusion that it is really a suboxide. However, Weintraub's paper does not contain a single complete analysis of the amorphous boron; and my own results and conclusions differ from his in certain important particulars.

In preparing the boron the mixture of magnesium and boron trioxide or borax was heated in a crucible through which a rapid current of hydrogen was passed. After cooling, the contents of the crucible were treated repeatedly with hot and moderately dilute hydrochloric acid. The product was then washed with water and dried in a desiccator. Finally, the powder was placed in a hard glass tube, which was connected with a mercury pump, and heated to the softening point of the glass. The following are the results of the analyses, and certain particulars with regard to the preparation of the various samples:

Composition of mixture.	I.	II.	III.	IV.
B ₂ O ₃	1	1	3	3
Mg	2½	2½	1	1
Time of heating.....	1 h. 20 m.	1 h. 20 m.	30 m.	30 m.

Analysis of Product.

Boron soluble in dilute nitric acid .	67.41	64.12	75.88	64.08
Boron insoluble in dilute nitric acid .	4.04	9.42	5.23	2.71
Mg	3.39	7.58	2.36	11.12
O (by difference) ...	25.16	18.88	16.53	22.09

Composition of mixture.	V.	VI.
Borax	1	5
Mg	1	4
Time of heating	1 h. 40 m.	1 h. 20 m.

Analysis of Product.

Boron soluble in dilute nitric acid.....	52.60	61.93
Boron insoluble in dilute nitric acid.....	20.94	3.90
Mg	7.63	9.97
O (by difference)	18.78	24.20

Weintraub does not appear to have made any distinction between the "amorphous boron," which is readily soluble in warm dilute nitric acid, and the crystalline boron, which is always present in smaller or larger quantity, and is insoluble in nitric acid. With regard to the magnesium content of the product he refers to the fact that samples containing less than 1 per cent. of magnesium had been obtained by heating mixtures of 4 parts of boron trioxide with 1 part of magnesium, and to the complete removal of the magnesium when the "boron suboxide is refused at high temperature with boric anhydride" in the electric vacuum furnace. The product then obtained is said to contain 16 to 14 per cent. of oxygen, but no analyses are given. This point will be discussed later.

The object of the present investigation was to obtain amorphous boron, which should be free from oxygen, and, therefore, samples of the substance containing oxygen were heated with excess of magnesium, and with metallic sodium. In the first case, magnesium boride was formed, and subsequently decomposed at the higher temperature employed. The final product in each case was crystalline boron, which was insoluble in nitric acid, and did not combine with magnesium to form a boride. The following are the results of the analysis of one sample of the crystalline boron:

Boron	98.10
Silicon	2.16
Magnesium	Trace
Total	100.26

It would appear that the substance which Weintraub considers to be boron suboxide, and has generally been supposed to be amorphous boron, is really a solid solution of a lower oxide of boron, in boron. This view is supported by the fact that, as Travers and Gupta have shown, an oxide, which has the formula $B_4O_3^*$ and is insoluble in acids or alkalis, actually exists, and also by the work of Louis (*Diss.*, Stuttgart), who has shown that the so-called monoxide of zirconium is possibly a solid solution of a dioxide in the amorphous element. It is not at all improbable that amorphous substances, which must be regarded as supercooled liquid, are only stable when they contain impurities. As will be shown presently, the magnesium in the substance is probably present as the oxide, possibly as a borite in solid solution. If this is assumed to be the case, the atomic ratio of the boron, which is soluble in nitric acid, to the oxygen which is not

combined with the magnesium, is found to have a fairly constant value:

No. of experiment.	I.	II.	III.	IV.	V.	VI.
Ratio B/O	4.2	6.6	6.6	6.1	5.2	5.2

One would expect the results to be more concordant if the substance were a compound, such as a suboxide. Further, the existence of an oxide, B_2O , does not appear to be likely.

Fairly conclusive evidence that the magnesium is present in combination with oxygen, and not in combination with boron, is derived from certain experiments, which were carried out with the view of testing Weintraub's statement that the magnesium could be removed by fusion with boron trioxide. Two samples of the amorphous boron were taken for these experiments, one of them containing a small, and the other a large, proportion of crystalline boron. The following are the results of the experiments:

Experiment A.

	Before fusing with boron trioxide.	After fusing with boron trioxide.
Boron insoluble in HNO_3	2.71	3.12
Boron soluble in HNO_3	64.08	77.35
Mg	11.12	0.58
O (by difference)	22.09	18.95
Ratio B/O (combined with B).....	6.10	6.02

Experiment B.

Boron insoluble in HNO_3	20.94	20.18
Boron soluble in HNO_3	52.60	58.41
Mg	7.68	3.23
O (by difference)	18.78	18.18
Ratio B/O (combined with B).....	5.20	5.30

In calculating the value of the ratio B/O (combined with B), it is assumed that the magnesium is present in both cases as the oxide MgO . As this ratio remains practically unchanged, even when nearly the whole of the magnesium has been removed, it is obvious that the removal of the magnesium must have been accompanied by the removal of oxygen, that these two elements were present in the system in combination, and that the magnesium was not present as a boride. That the magnesium is not removed by heating the amorphous boron with hydrochloric acid in a sealed tube to 150° , whilst it is readily removed by fusion with boron trioxide, may be explained by the fact that the rate of diffusion of the magnesium oxide in the "solid" solution is very much greater at the higher than at the lower temperature.

It should, furthermore, be pointed out that on heating the samples of boron which were prepared from borax they evolved

a considerable quantity of hydrogen, but that the loss of weight on heating was only equivalent to the weight of hydrogen lost. The atomic ratio of the hydrogen to the total oxygen is in the first case 1/1.3 and in the second case 1/3. In both cases the atomic ratio of the boron soluble in nitric acid to the total oxygen is the same, namely, 5.2, and this, together with the fact that the loss of weight is equal to the weight of the hydrogen lost, makes it probable that the hydrogen is actually occluded in the substance, and is not originally present as water. Thus from 1 gram of substance there was obtained, in the case of No. V, 0.009 gram of hydrogen, and 0.004 gram in the case of No. VI. The samples of boron prepared from boron trioxide gave off only a trace of gas.

It will be observed that both the samples of amorphous boron which yield hydrogen on heating contain a large quantity of crystalline boron, and that it is the crystalline boron which occludes the hydrogen appears, from the following experiment, to be highly probable. A quantity of amorphous boron, containing about 3 per cent. of crystalline boron, which yielded only a trace of hydrogen when heated, was heated strongly with a small quantity of magnesium, and the residue, after treating with hydrochloric acid, and washing with water, was dried in a vacuum overnight. The residue, containing 30 per cent. of crystalline boron, was dried in a desiccator for a day, and the quantity of hydrogen which was given off on heating was determined. Further determinations of the quantity of hydrogen evolved on heating were made after sixteen and seventy-two days. The following are the results of the experiments:

Time.	Quantity of hydrogen per cent.
1 day.....	0.52
16 days	0.46
72 "	0.34

As might be expected the occluded hydrogen is slowly oxidised when the boron is exposed to the air.

Magnesium Boride.

As it was found that no change took place when crystalline boron was heated with magnesium, that it was impossible to obtain amorphous boron free from oxygen, and that magnesium boride decomposed when heated strongly into magnesium and boron, it was obviously impossible to obtain the boride in the pure state, but only a mixture of the boride with magnesium oxide and a small quantity of crystalline boron. However, by investigating the reaction between magnesium and the amorphous boron, and

making a series of analyses of the products, it was possible to arrive at a definite conclusion as to the composition of the one boride which appears to exist.

In these experiments the samples of amorphous boron I and III, of which the analyses are given above, were employed. The brown powder was packed tightly between two layers of magnesium powder into the magnesia-lined iron crucible. The cover was then screwed on to the crucible, which was heated to a red heat for about half-an-hour, a rapid current of hydrogen being passed into it from the commencement of the experiment until the apparatus was cold. The crucible was then opened, and the mass of boride was separated without difficulty from the two plates of metallic magnesium which lay above and below it. It was then crushed and analysed. The following are the results of the analyses:

	I.	II.	III.	IV.	V.
Insoluble in nitric acid.....	3.32	2.42	1.03	0.76	0.76
Insoluble in hydrochloric acid .	3.86	2.48	1.10	0.80	—
Magnesium	70.16	74.48	73.33	72.99	74.13
Boron soluble in nitric acid.....	17.19	14.82	16.76	18.48	18.76
Oxygen (by difference)	8.83	8.28	8.88	7.77	6.35
Magnesium as oxide	13.23	12.42	13.32	11.64	9.51
Magnesium as boride, or as metal					
(A)	56.93	62.06	60.01	61.35	64.62
Boron as boride (B)	17.19	14.82	16.76	18.48	18.76
Ratio A/B	1.5/1	1.9/1	1.6/1	1.5/1	1.5/1

In this series of experiments it will be observed that the difference between the amount of the residue insoluble in nitric acid and of the residue insoluble in hydrochloric acid is extremely small, showing that the whole of the boron was present either as boride, or as crystalline boron. It is, therefore, certain that not more than 1.5 gram-atoms of magnesium is required to combine with 1 gram-atom of boron. Further, when the ratio A/B rose much above 1.5, as in the case of experiment No. II, the residue had a metallic appearance, and obviously contained metallic magnesium.

In order to determine whether a boride containing less magnesium than the compound Mg_3B_2 could exist under the conditions under which these experiments were carried out, samples of product No. II were heated for increasing periods in a vacuum in quartz tubes. The following are the results of the experiments:

	II.	IIa.	IIb.	IIc.
Insoluble in nitric acid.....	2.42	2.51	4.60	8.55
Insoluble in hydrochloric acid.....	2.48	2.48	6.30	12.23
Magnesium	74.48	72.44	68.02	63.10
Boron soluble in nitric acid	14.82	15.16	16.65	15.23
Oxygen (by difference)	8.28	9.89	10.73	13.12
Mg as oxide	12.42	14.82	16.08	19.68
Mg as boride or as metal (A)	62.06	57.62	51.94	43.42
B as boride (B)	14.82	15.16	14.90	13.55
Ratio A/B	1.9/1	1.7/1	1.59/1	1.47/1

The results of these experiments show that on heating in a vacuum such a mixture, for which the value of the ratio A/B is much greater than 1.6, magnesium volatilises, but that, at first, the quantity of free boron does not increase. When, however, the value of the ratio falls to the neighbourhood of 1.5, the quantity of crystalline and amorphous boron in the mixture begins to increase rapidly. It may, therefore, be concluded that under the conditions of temperature and pressure at which the experiment was carried out, no boride of magnesium other than the compound Mg_3B_2 can exist.

Conclusions.

(1) The element boron has only been obtained in one form in a state approaching purity, namely, that of a crystalline substance which is practically insoluble in nitric acid.

(2) Weintraub's conclusion that the so-called amorphous boron always contains a considerable quantity of oxygen has been confirmed.

(3) It appears probable that the so-called amorphous boron is a solution of a lower oxide of boron and of magnesium oxide, possibly in combination as a borite, in elementary boron in the amorphous or superfused liquid state. The magnesium oxide may be removed by fusion with boron trioxide, but not by heating with acids.

(4) On heating crystalline boron with magnesium no reaction takes place, but on heating the so-called amorphous boron with magnesium, a mixture of magnesium boride (Mg_3B_2) and magnesium oxide is obtained.

(5) At a red heat and under normal pressure only one boride having the formula Mg_3B_2 is formed.

(6) On heating the boride, magnesium is driven off and the greater part of the boron separates in the crystalline state.

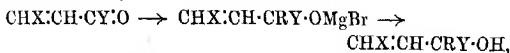
DEPARTMENT OF GENERAL CHEMISTRY,
INDIAN INSTITUTE OF SCIENCE,
BANGALORE, INDIA.

CCl.—*The Action of Magnesium Phenyl Bromide on Derivatives of Phenyl Styryl Ketone.*

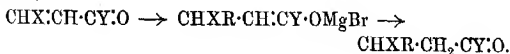
By IDA SMEDLEY MACLEAN and SIBYL TAITE WIDDOWS.

IN an investigation which had for its object the preparation of an optically active compound, we desired as starting materials the *p*-carbethoxy- and *p*-dimethylamino-derivatives of $\beta\beta$ -diphenyl-propiophenone. It was expected that these substances would be produced by the action of magnesium phenyl bromide respectively on the *p*-carbethoxy- and *p*-dimethylamino-derivatives of phenyl styryl ketone. These reactions have therefore been carried out and the products investigated. As the behaviour of these substances in subsequent reactions did not lead to the results anticipated, it has been found necessary to modify our original scheme, and we desire therefore at this stage to record the properties of the substances prepared in the course of this investigation.

The action of unsaturated ketones with the Grignard reagent has been extensively studied by Kohler and his co-workers. He finds that in compounds containing the grouping $>C:C\dot{C}:O$, the addition of the magnesium compound may take place in two ways, namely, (a) by $\alpha\beta$ -addition, leading to the formation of an unsaturated alcohol,



or (b) by $\alpha\delta$ -addition, leading to the formation of a saturated ketone,

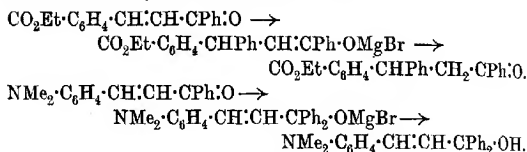


As the result of the investigation of a large number of these compounds, Kohler (*Amer. Chem. J.*, 1907, **38**, 511) concludes that the mode of addition to substances containing the chain $>C:C\dot{C}:O$ is affected more by the number and arrangement of the hydrocarbon residues in the ketone than by their chemical character; on the other hand, the relation between the mode of addition and the nature of the magnesium compound is less easily determined, but from the results obtained by the action of various magnesium compounds on styryl ethyl ketone, Kohler suggests that the mode of addition to any given ketone depends more on the chemical than on the spatial character of the hydrocarbon residues contained in the magnesium compound.

The action of magnesium phenyl bromide on phenyl styryl

ketone was investigated by Kohler (*Amer. Chem. J.*, 1903, 29, 352; 1904, 31, 642), who showed that the product consisted of diphenylpropiophenone. Addition of the magnesium compound had therefore taken place in the $\alpha\beta$ -position.

We expected, therefore, that the action of magnesium phenyl bromide on phenyl *p*-carbethoxystyryl ketone and on phenyl *p*-dimethylaminostyryl ketone would take place similarly, and that in each case the saturated ketone would be formed. The possibility that the carbethoxy-group in the benzene nucleus might also react was not excluded, and a diminished yield of the desired ketone in this event might be expected. We find, however, that whereas the main product of the reaction with phenyl *p*-carbethoxystyryl ketone is a saturated ketone (the reaction being therefore similar to that with phenyl styryl ketone itself), in the case of phenyl *p*-dimethylaminostyryl ketone the product is unsaturated, and the addition of the magnesium compound appears therefore to have taken place in this case in the $\alpha\beta$ -position, the final product being the unsaturated alcohol.



In the case of the substances now investigated, therefore, the chemical nature of the substituent appears to exercise a considerable influence on the mode of addition, and the electronegative character of the groups to be a factor of considerable importance in determining whether addition shall take place in the $\alpha\beta$ - or the $\alpha\delta$ -position. In each case the carbethoxy- and dimethylamino-groups occupy the para-position, and the difference in the size of the groups $\cdot\text{C}_6\text{H}_4\text{NMe}_2$ and $\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$ can hardly be sufficient to account for the marked difference in the nature of the reaction observed. It seems difficult, therefore, to explain the results now described by the phenomenon of steric hindrance, the chemical nature of the substituents in the phenyl nucleus being here, apparently, a factor of considerable importance.

We propose to investigate further the effect of the substituted amino-group on the reaction of unsaturated ketones with the Grignard reagent.

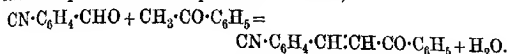
EXPERIMENTAL.

The *p*-cyanobenzaldehyde required for the preparation of phenyl *p*-carbethoxystyryl ketone was obtained from toluene by the

series of reactions previously carried out by Mellinghoff (*Ber.*, 1889, **22**, 3208) and Reinglass (*Ber.*, 1891, **24**, 2421), employing the improved method of oxidation of Moses (*Ber.*, 1900, **33**, 2624)

Phenyl p-Cyanostyryl Ketone.

This compound was prepared by condensing *p*-cyanobenzaldehyde with acetophenone in the presence of alkali,



Sixteen grams of *p*-cyanobenzaldehyde were dissolved in 150 c.c. of alcohol, and 15 grams of acetophenone added. The alcoholic solution was heated to 40°, and 20 grams of a 10 per cent. solution of sodium hydroxide were added, the whole being well stirred. The solution became deep yellow, and almost immediately the condensation product began to separate. The solid was collected and washed with alcohol, when 26 grams of the crude product were obtained, being a yield of 90 per cent. of the theoretical. After three recrystallisations the substance separated in colourless masses of branched needles, and melted at 156—157°:

0.1720 gave 0.5190 CO₂ and 0.0784 H₂O. C=82.38; H=5.06.

0.1940 „ 10.2 c.c. N₂ (moist) at 14° and 761.5 mm. N=6.2.

C₁₆H₁₁ON requires C=82.40; H=4.72; N=6.0 per cent.

On allowing the mother liquor obtained from the crude phenyl-*p*-cyanostyryl ketone to remain, a small amount of a colourless substance separated, which was not further investigated.

Phenyl p-Carboxymethylstyryl Ketone,



The hydrolysis of the cyano-group and the esterification of the carboxyl group were effected by passing a current of hydrogen chloride through a hot alcoholic solution of phenyl *p*-cyanostyryl ketone.

Ten grams of this compound were dissolved in about 200 c.c. of methyl alcohol in a flask fitted with a reflux condenser, and into this solution, heated on a water-bath, a current of dry hydrogen chloride was passed for eight hours. On remaining overnight a crystalline precipitate separated, which, when recrystallised twice from alcohol, gave colourless needles, sparingly soluble in ether, and melting at 121—122°:

0.1884 gave 0.5320 CO₂ and 0.0848 H₂O. C=77.01; H=4.99.

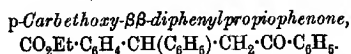
0.1913 „ 0.5358 CO₂ „ 0.0898 H₂O. C=76.38; H=5.21.

C₁₇H₁₄O₃ requires C=76.69; H=5.26 per cent.

Similarly, the *ethyl* ester was prepared from the solution of the ketone in ethyl alcohol. After twice recrystallising from alcohol, colourless plates, melting at 83–84°, were obtained. These were rather more soluble in ether than the corresponding methyl ester:

0.1527 gave 0.4344 CO₂ and 0.0800 H₂O. C=77.50; H=5.81.

C₁₈H₁₆O₃ requires C=77.14; H=5.71 per cent.



This substance was prepared by the action of magnesium phenyl iodide on phenyl *p*-carbethoxystyryl ketone. As the result of a large number of experiments, in which the proportion of the Grignard reagent was varied, it was found that the best result was obtained when two molecules of magnesium phenyl bromide were taken to one molecule of the ketone. With one molecule of the Grignard reagent, a considerable part of the ketone remained unattacked, whilst the yield of the product was not improved by adding a larger excess of the Grignard reagent. The reaction was also carried out in benzene and in amyl ether solution, but the results were less successful than with ether. It was found most advantageous to add the Grignard reagent to the ethereal solution or suspension of the ethyl ester, heated on the water-bath.

Ten grams of the ethyl ester were added to 150 c.c. of ether, and the solution was warmed on the water-bath; magnesium phenyl iodide, prepared from 5.64 grams of magnesium and 15.5 grams of iodobenzene, was slowly run in with constant shaking. (Three times the calculated quantity of magnesium was taken, as recommended by McKenzie and Martin, T., 1913, **103**, 113, and Schmidlin and Massini, *Ber.*, 1909, **42**, 2381.) After the addition of the Grignard reagent, the heating was continued for about three-quarters of an hour, when the product was decomposed by the addition of ice and dilute sulphuric acid, and the ethereal solution separated. After distilling off the ether, the residue was distilled in a current of steam to remove excess of iodobenzene and diphenyl. The product, after steam distillation, was extracted with ether, the ethereal solution dried and distilled, and the residue left over sulphuric acid in a vacuum desiccator. The yellow, viscous mass was very soluble in all the ordinary organic solvents, and resisted all attempts at crystallisation.

Analysis of different specimens of the substance obtained under different conditions gave the following results:

C=81.6, 82.07, 82.48, and 81.6. H=6.20, 6.20, 6.18, and 6.14.

C₂₄H₂₂O₃ requires C=80.44; H=6.14 per cent.

The viscous substance was therefore not pure, and probably contained small quantities of other by-products capable of being formed by the Grignard reagent reacting with more than one group of the molecule.

The viscous mass, containing *p*-carbethoxy- $\beta\beta$ -diphenylpropio-phenone, was heated with a 10 per cent. solution of alcoholic potassium hydroxide on a water-bath for ten minutes. The alcohol was distilled off, the residue cooled, diluted, and filtered from a slight amount of oily substance. To the filtrate was added excess of dilute hydrochloric acid, when a white precipitate of the corresponding acid separated. This was dissolved in sodium carbonate solution, from which the sparingly soluble sodium salt separated. This forms silky needles, melting at 124–125°. The potassium salt is also sparingly soluble, but dissolves more readily than the sodium salt.

The acid, reprecipitated from the salt and crystallised from dilute alcohol, separated in clusters of transparent needles, melting at 184–185°. The yield of purified acid was between 10 and 15 per cent. of the theoretical amount:

0.1235 gave 0.3624 CO_2 and 0.0651 H_2O . $\text{C}=80.29$; $\text{H}=5.84$.

$\text{C}_{22}\text{H}_{18}\text{O}_3$ requires $\text{C}=80.00$; $\text{H}=5.45$ per cent.

The molecular weight was determined by ignition of the silver salt:

0.4666 gave 0.1554 Ag. M.W. = 329.67.

$\text{C}_{22}\text{H}_{18}\text{O}_3$ requires M.W. = 330.

The formation of a *semicarbazide* showed that the carbonyl group was also present.

The acid (0.4 gram) was heated in alcoholic solution with the calculated quantity of semicarbazide hydrochloride and sodium acetate. After some time a white precipitate separated, which melted at 216–217°. It was sparingly soluble in alcohol, benzene, or ether, and was best recrystallised from acetone. The purified substance melted and decomposed at 220–221°:

0.1146 gave 0.3004 CO_2 and 0.0584 H_2O . $\text{C}=71.49$; $\text{H}=5.60$.

0.0704 „ 6.7 c.c. N_2 (moist) at 19° and 758 mm. $\text{N}=10.92$.

$\text{C}_{23}\text{H}_{21}\text{O}_4\text{N}_3$ requires $\text{C}=71.31$; $\text{H}=5.42$; $\text{N}=10.85$ per cent.

The acid, when tested with bromine in alcoholic solution and with potassium permanganate solution, behaved as a saturated compound.

Phenyl p-Dimethylaminostyryl Ketone.

This compound was prepared by condensing *p*-dimethylamino-benzaldehyde with acetophenone in the presence of sodium methoxide in alcoholic solution.

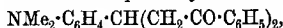
Equimolecular proportions of *p*-dimethylaminobenzaldehyde and acetophenone were dissolved in alcohol, and one molecular proportion of sodium methoxide in methyl-alcoholic solution was added. The whole was heated for a few minutes and allowed to remain overnight, when a copious mass of the condensation product separated. On recrystallisation from alcohol, orange-coloured crystals were obtained, melting at 113—114° (compare Sachs and Lewin, *Ber.*, 1905, **35**, 3576). From the mother liquors two other substances were isolated; after the removal of the greater part of phenyl *p*-dimethylaminostyryl ketone, pale yellow crystals separated, which on repeatedly recrystallising from alcohol were obtained in colourless, glistening crystals, melting at 124—125°. These are not described as occurring in the preparation of phenyl *p*-dimethylaminostyryl ketone given by Sachs and Lewin (*loc. cit.*):

0.1880 gave 0.5596 CO₂ and 0.1116 H₂O. C=81.17; H=6.59.

0.1793 „ 6.4 c.c. N₂ (moist) at 11° and 750 mm. N=4.20.

C₂₅H₂₅O₂N requires C=80.86; H=6.73; N=3.77 per cent.

The substance has therefore probably the constitution



being formed by the condensation of two molecules of acetophenone with one molecule of dimethylaminobenzaldehyde. It failed, however, to give a semicarbazide when warmed with the equivalent quantities of semicarbazide hydrochloride and sodium acetate. The remaining substance which was separated was formed only in small amount; it was insoluble in alcohol, and has not been further investigated.

Diphenyl-p-dimethylaminostyrylcarbinol,
 $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{CPh}_2 \cdot \text{OH}.$

This substance was prepared by the action of magnesium phenyl bromide on phenyl *p*-dimethylaminostyryl ketone. It was found that the best result was obtained by adding a large excess of the Grignard reagent (three times the calculated amount) to the amino-compound dissolved or suspended in boiling ether. The reaction seemed to be complete at the end of about one hour, the ethereal solution being kept boiling throughout.

On first adding the Grignard reagent a crimson colour was produced, which gradually disappeared as the reaction progressed, until finally a nearly colourless solution was obtained. The mixture was then cooled, and ice and dilute sulphuric acid were added. On addition of the acid a violet colour was produced, and the liquid separated into three layers, namely, (1) an ethereal, (2) an aqueous, and (3) a deep red, oily layer. The latter, which was

insoluble in ether, contained the sulphate of the product required. It was several times shaken with ether to remove the excess of bromobenzene and any diphenyl formed. On allowing the oil so obtained to remain in contact with dilute sulphuric acid, *diphenyl-pdimethylaminostryrylcarbonyl sulphate* separated in colourless, shining plates. If the oil is at once treated with excess of sodium carbonate solution, the free base separates as a white solid. This was extracted with ether, the ethereal solution dried and evaporated, and the yellowish-white solid which was left recrystallised several times from alcohol. It was also purified by distillation under diminished pressure; a yellow, viscous liquid passed over at 297–300°/15 mm., which solidified on cooling to a yellow solid, and after three recrystallisations from alcohol this furnished colourless needles, melting at 100°. The yield was 37 per cent. of the theoretical:

0.1894 gave 0.5846 CO₂ and 0.1220 H₂O. C=84.17; H=7.15.

0.1314 „ 5.25 c.c. N₂ (moist) at 16° and 768.4 mm. N=4.7.

C₂₀H₂₈ON requires C=83.89; H=6.99; N=4.25 per cent.

The above substance failed to give a semicarbazide. In alcoholic solution, one molecular proportion of bromine was readily absorbed at the ordinary temperature. In acid solution it readily decolorised a solution of potassium permanganate in the cold, and in alcoholic solution rapidly reduced a cold, neutral solution of permanganate. The substance therefore contains an ethylenic linking, and must be regarded as the unsaturated alcohol. The red colour produced by the addition of sulphuric acid to the product of the Grignard reaction is evidently due to a trace of an impurity, as the purified base gives no colour when treated with dilute sulphuric acid. Traces of a by-product formed in the reaction also produce a green fluorescence in chloroform solution, a property which is not shown by the purified base.

The expense of this research has been in part defrayed by a grant from the Royal Society, for which we desire to express our thanks.

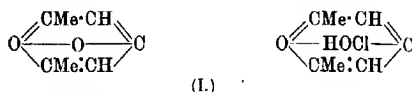
BIOCHEMICAL DEPARTMENT,
LISTER INSTITUTE.

CHEMICAL DEPARTMENT,
LONDON SCHOOL OF MEDICINE
FOR WOMEN.

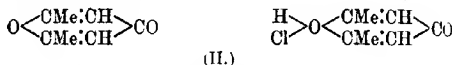
CCII.—*The Constitution of the Arylidenedimethylpyrones and their Salts.*

By ALFRED ARCHIBALD BOON, FORSYTH JAMES WILSON, and
ISIDOR MORRIS HEILBRON.

THE constitution of 4-pyrone, the alkylpyrones and the salts which these substances form with acids has been fully investigated, both from the chemical and from the spectrographic point of view. From purely chemical considerations Collie (T., 1904, 85, 973) was led to adopt a bridged formula for dimethylpyrone and its hydrochloride:



in place of the formulæ:



which were at that time generally ascribed to the base and its hydrochloride.

The spectrographic investigations of these substances by Baly, Collie, and Watson (T., 1909, 95, 144) also favoured bridged formulæ for the pyrones and their salts with acids. If dimethylpyrone possessed the unsaturated structure as represented by formula II, it would be expected to show strong selective absorption: a glance at Fig. 1 (dash curve I), where we have reproduced the absorption curve of dimethylpyrone, shows that the absorption is merely of a general character, which is in agreement with the bridged structure for this compound.

On the other hand, the absorption of the pyrones in the presence of sodium ethoxide and also the alcohol compound of dimethylpyrone (Fig. 1, dash curve II), exhibit strong selective absorption. In order to account for these changes, the additive compounds are represented by the following formulæ:



In a recent paper (P., 1914, 30, 205) one of us has shown that dimethylpyrone can be condensed with aldehydes forming arylidenedimethylpyrones, coloured basic compounds, from which, by the action of acids, intensely coloured salts can be obtained.

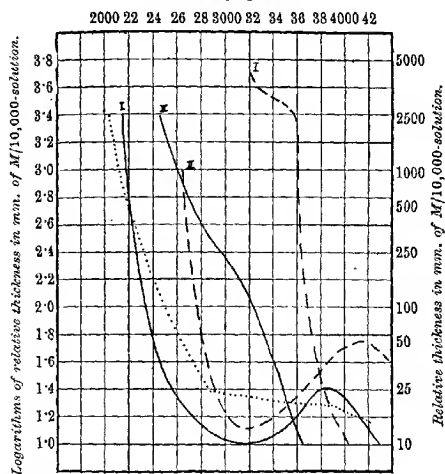
A spectrographic examination of these arylidenedimethylpyrones and their salts has been undertaken, and also that of bis($\alpha\beta$ -di-

bromoanisylmethylpyrone, the preparation of which is described at the end of this paper. The results of this investigation throw light, we believe, on the constitution of the various compounds in question, and indicate also the nature of the reaction taking place when dimethylpyrone is condensed with an aldehyde in the presence of an alcoholic solution of sodium hydroxide.

Figs. 1 and 2 show the absorption curves of these aryledenedimethylpyrones. All are very similar in type, a broad, well-defined

FIG. 1.

Oscillation frequencies.



Full curve I.: Bis(anisylidene-methyl)pyrone in alcohol.

" " II.: Tetrabromo-derivative in alcohol.

Dot curve: " " " " + excess of sodium ethoxide.

Dash curve I.: Dimethylpyrone (reproduced).

" " II.: Alcohol compound of dimethylpyrone (reproduced).

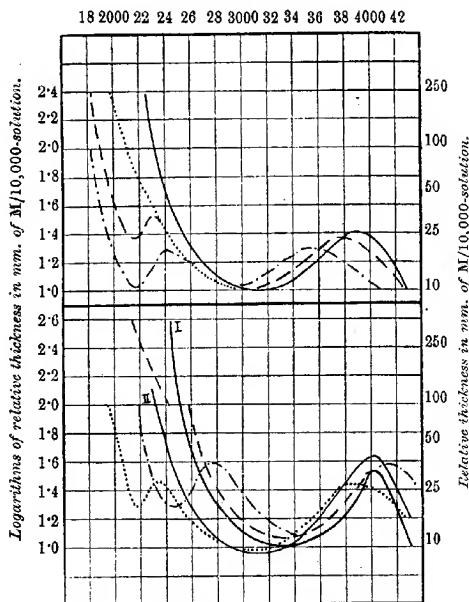
band with head at $1/\lambda$ 3000—3200 being exhibited by each in $M/10,000$ -solution. It will be seen, moreover, from Fig. 1 that the absorption curves of these pyrones are similar to that obtained by Baly, Collie, and Watson (*loc. cit.*) for the alcohol compound of dimethylpyrone, the higher degree of unsaturation and the greater molecular weights of the aryledenedimethylpyrones accounting for the shift towards the red end of the spectrum. Hence, we are forced to the conclusion that whilst dimethylpyrone doubtless possesses a

bridged structure, the compounds examined by us are of the symmetrical unsaturated type:



FIG. 2.

Oscillation frequencies.



Upper curves.

- Full curve : *Bis(anzylidenemethyl)pyrone in acetic acid.*
 Dot " : *Formate in alcohol.*
 Dash " : *Hydrochloride in alcohol.*
 Dot and dash curve : " " *chloroform.*

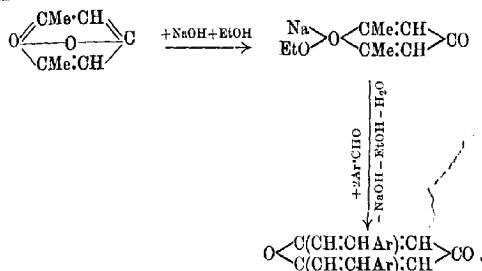
Lower curves.

- Full curve I : *Bis(benzylidenemethyl)pyrone in alcohol.*
 Dash curve : *Hydrochloride in alcohol.*
 Dot and dash curve : *Bis(benzylidenemethyl)pyrone in sulphuric acid.*
 Full curve II : *Bis(furfurylidenemethyl)pyrone in alcohol.*
 Dot curve : *Hydrochloride in alcohol.*

In order to explain the mechanism of the condensation of dimethylpyrone with aldehydes in the presence of alcoholic sodium

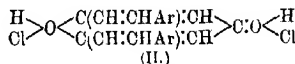
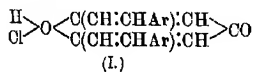
hydroxide, the first action appears to be the formation of the sodium ethoxide compound of dimethylpyrone, a symmetrical structure being thereby produced.

In consequence of the symmetry of the molecule both of the methyl groups are simultaneously attacked by the aldehyde, with the production of a bis(arylidene-methyl)pyrone. As already indicated in the previous paper, all attempts to cause only one methyl group to react with a given aldehyde were unsuccessful, and this can be explained only on the assumption of a symmetrical structure of the molecule. The following scheme would represent according to our views the course of this reaction:



It is noteworthy that Staudinger ("Die Ketene," Stuttgart, pp. 63, 115) found that, owing to the presence of the carbonyl group, dimethylpyrone reacts with diphenylketene, although with difficulty.

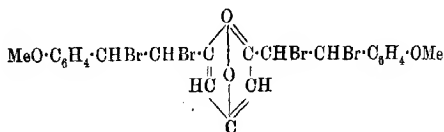
The spectrographic examination of the salts formed by the action of acids on these arylidenedimethylpyrones has led us to the conclusion that these salts have a constitution quite similar to that of the parent compounds. The hydrochloride, for example, would be represented by the formula I, but it should be noted that with excess of hydrochloric acid a dihydrochloride (II) might possibly be formed.



In Fig. 2 (upper curves) are shown the absorption spectra of bis(arylidene-methyl)pyrone in alcohol, and also the curves of various salts of this substance. In the presence of acetic acid no alteration in the absorption takes place, whilst, on the other hand, the hydrochloride of this substance shows two absorption bands,

one practically identical with that exhibited by the parent substance and one of very small persistence with head at $1/\lambda$ 2200, to which may be assigned the characteristic colour of the salt. It was found when examining these salts in alcoholic solution that a large excess of acid was necessary to ensure complete salt-formation and obtain the two bands. The absorption curve of the sulphuric acid salt is similar to that of the hydrochloride, whilst the yellow formate (dot curve) shows an absorption curve with only one band, but further into the red than the acetate. The lower curves represent the absorption spectra of bis(furfurylidene)methylpyrone, bis(benzylidene)methylpyrone, and some of their salts. In the case of the latter compound, which is evidently less basic than either of the other two pyrones, complete salt-formation with appearance of the two characteristic bands was obtained in photographing only in pure sulphuric acid.

The addition of four atoms of bromine to the unsaturated side-chains in bis(anisylidene)methylpyrone produces a very marked change in the type of absorption curve, as is evident from a glance at Fig. 1. It will, moreover, be seen that as regards general absorption this tetrabromo-derivative corresponds with dimethylpyrone, hence we ascribe the bridged structure:

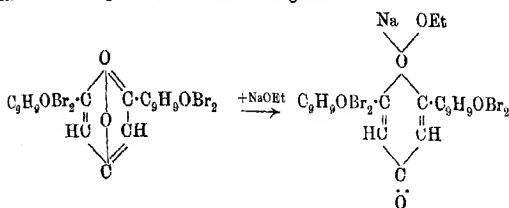


to this compound.

So far no salts with acids have been obtained from this substance, and the addition of hydrochloric acid produced no alteration in the absorption curve; the presence of the bromine atoms evidently tends to make the whole molecule too acidic for salt formation with acids. A similar case is afforded by diacetyldimethylpyrone, which, as was pointed out by Collie (T., 1904, 85, 971), yields no salts with acids. It would seem, therefore, that the bridged structure is possessed by pyrones of an acidic or weakly basic nature; thus, according to Baly, Collie, and Watson (*loc. cit.*), dimethylpyrone, diacetyldimethylpyrone, and ethyl chelidonate all possess the bridged structure. On the other hand, the arylidene-dimethylpyrones examined by us are undoubtedly more basic, easily yielding, as they do, salts with acids, and we venture to suggest that it is the basic character which conditions the symmetric structure.

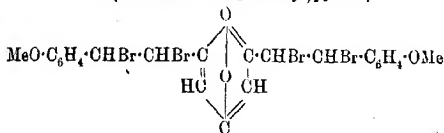
A further proof that the arylidenedimethylpyrones are more basic

than any compounds of this type hitherto examined is afforded by the fact that bis(anisylidenemethyl)pyrone apparently yields no compound with sodium ethoxide; even a large excess of this reagent produced no change in the absorption curve. The tetrabromo-additive compound, however, being acidic, gave indications of the formation of a sodium ethoxide compound; the absorption curve in presence of a large excess of sodium ethoxide is shown in Fig. 1 (dot curve), where it will be noticed there is a large step-out in the same position as the characteristic band of the bis(arylidenemethyl)pyrone. An alteration from the bridged to the open unsaturated structure as expressed in the following scheme:



would account for the change in the absorption curve, and would be paralleled by the change which dimethylpyrone undergoes in the presence of a large excess of sodium ethoxide.

Bis(αβ-dibromoanisylmethyl)pyrone,



Two grams of the parent substance were dissolved in 40 c.c. of dry chloroform, and to this solution an amount of dry bromine far in excess of the calculated quantity was gradually added. On the solvent being allowed to evaporate gradually in a current of dry air a red cake was obtained. This was ground with alcohol, and then heated on a water-bath after the addition of more alcohol. An oil was thus collected, which solidified after some time. The solid was ground up, washed well with alcohol, and dried on a porous plate:

0.1306 gave 0.1448 AgBr. Br=47.12.

$\text{C}_{28}\text{H}_{20}\text{O}_4\text{Br}_4$ requires Br=47.05 per cent.

This tetrabromo-derivative is a yellow, amorphous compound, which melts and decomposes at 134–136°.

One of us (Boon) is continuing this investigation, more particularly in reference to a study of the action of bromine on arylidene-dimethylpyrones and a refractometric examination of some of these pyrones and their derivatives.

CHEMISTRY DEPARTMENT,
HERIOT-WATT COLLEGE,
EDINBURGH.

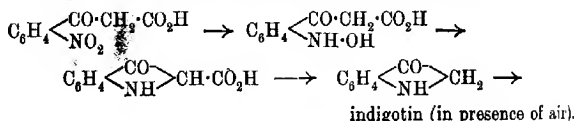
CHEMISTRY DEPARTMENT,
ROYAL TECHNICAL COLLEGE,
GLASGOW.

CCIII.—*p*-Toluoylacetic Acid, *o*-Nitro-*p*-toluoylacetic Acid, and 6:6'-Dimethylindigotin.

By JAMES COOPER DUFF.

THE work described in this paper is similar to that on *o*-nitrobenzoylacetic acid by Needham and Perkin (T., 1904, 85, 148), in which it was unexpectedly found that when ethyl *o*-nitrobenzoylacetoacetate is warmed with concentrated sulphuric acid and then poured on ice, *o*-nitrobenzoylacetic acid was obtained, and not ethyl isatogenate as was expected. The sulphuric acid apparently produced no internal condensation between the nitro-group and the methylene radicle.

Since then Perkin has found (private communication) that when *o*-nitrobenzoylacetic acid is dissolved in dilute sodium hydroxide solution and reduced with zinc dust it gives a quantitative yield of indigotin. Probably the reaction proceeds in stages as follows:



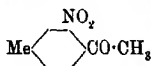
It was at Prof. Perkin's suggestion that this work on the preparation of the corresponding nitro-*p*-toluoylacetic acid was started with a view to obtain 6:6'-dimethylindigotin:



Ethyl o-nitro-*p*-toluoylacetate was prepared by condensing *o*-nitro-*p*-toluoyl chloride with the sodium compound of ethyl acetoacetate, and then hydrolysing the resulting sodium derivative of ethyl *o*-nitro-*p*-toluoylacetoacetate with dilute ammonia solution and ammonium chloride. The ester is a colourless, crystalline solid,

and on hydrolysis gives an almost quantitative yield of *o*-nitro-*p*-toluoylactic acid.

This acid loses carbon dioxide when boiled with water, and gives a very good yield of *o*-nitro-*p*-tolyl methyl ketone,



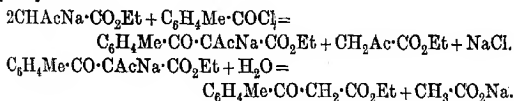
as a yellow oil.

When *o*-nitro-*p*-toluoylactic acid is dissolved in dilute sodium hydroxide solution and warmed with zinc dust it is converted into 6:6'-dimethylindigotin. It thus behaves like *o*-nitrobenzoylactic acid.

6:6'-Dimethylindigotin has been prepared previously by Kuhara and Chikashigé (*Amer. Chem. J.*, 1902, **27**, 1) from chloroaceto-*m*-toluidide by fusion with potassium hydroxide. It is very similar to indigotin in its properties and its appearance, being slightly more soluble in solvents.

It was found that *p*-toluoylactic acid and its ethyl ester had not been prepared by Claisen's method as used for ethyl benzoylacetate (*Annalen*, 1896, **291**, 67). It was therefore thought worth while to include their preparation in this paper. They have been obtained previously by Marguery (*Bull. Soc. chim.*, 1905, [iii], **33**, 548) by Friedel and Crafts' reaction from toluene and the mono-ethyl ester of malonic acid.

In their preparation by Claisen's method *p*-toluoyl chloride was condensed with the sodium derivative of ethyl acetoacetate, and the resulting sodium derivative of ethyl *p*-toluoylacetate was hydrolysed:



A good yield of ethyl *p*-toluoylacetate is obtained, and it readily gives *p*-toluoylactic acid on hydrolysis.

EXPERIMENTAL.

Ethyl o-Nitro-*p*-toluoyl Acetate.

It was necessary to prepare first *o*-nitro-*p*-toluic acid. This was done by nitrating aceto-*p*-toluidide following directions given by Beilstein and Kuhlberg (*Annalen*, 1870, **155**, 23), and then converting the *o*-nitro-*p*-toluidine into *o*-nitro-*p*-toluonitrile by Sandmeyer's reaction. The nitrile was hydrolysed to *o*-nitro-*p*-toluic acid by heating at 150—160° with 6 parts of concentrated hydro-

chloric acid for eight hours (Noyes, *Amer. Chem. J.*, 1888, 10, 472).

A mixture of *o*-nitro-*p*-toluic acid (100 grams) and phosphorus pentachloride (105 grams) was gently warmed until reaction ceased, and the phosphoryl chloride was distilled off at the lowest possible temperature. The *o*-nitro-*p*-toluoyl chloride remained as a mass of small needles.

Ethyl acetoacetate (66 grams) was mixed with 180 c.c. of sodium ethoxide solution (23 grams of sodium in 360 c.c. of alcohol), the whole cooled to 0°, and 40 grams of *o*-nitro-*p*-toluoyl chloride were added in small quantities at a time and with frequent stirring, so that the temperature remained below 5°. After half an hour 90 c.c. of the sodium ethoxide solution and 20 grams of the acid chloride were added under the same conditions as before. The whole was then left for half an hour and treated with the rest of the sodium ethoxide and 20 grams of the acid chloride. After remaining overnight, the yellow precipitate, which consisted of the sodium compound of ethyl *o*-nitro-*p*-toluoylacetacetate and sodium chloride, was collected and washed, first with alcohol and then with ether.

Part of this sodium compound was added to excess of dilute hydrochloric acid, cooled by the addition of powdered ice, and the whole shaken thoroughly with ether. The ethereal solution was washed with a dilute aqueous solution of sodium hydrogen carbonate, dried, and evaporated. A yellow oil remained, which crystallised in plates after some minutes, and consisted of ethyl *o*-nitro-*p*-toluoylacetacetate. The alcoholic solution gives a reddish-violet coloration with ferric chloride:

0.2776 gave 11.5 c.c. N_2 at 22° and 750 mm. $N=4.6$.

$C_{14}H_{15}O_6N$ requires $N=4.8$ per cent.

For preparing ethyl *o*-nitro-*p*-toluoylacetate, the crude sodium compound obtained above, in quantities of 100 grams, was mixed with 25 grams of ammonium chloride and 500 c.c. of water. Ten c.c. of concentrated aqueous ammonia, diluted with 90 c.c. of water, were then added, and the whole was stirred vigorously at 35–40° until all the sodium compound had dissolved. The solution was cooled and acidified with hydrochloric acid after the addition of ice, when a pale brown oil separated, which soon solidified. This was extracted with ether, and the ethereal solution shaken with a solution of the blue cuprammonium compound, prepared by adding ammonia in slight excess to concentrated copper sulphate solution. A deep green copper derivative separated almost completely after a few minutes' shaking, which was collected and washed, first with water and then with ether.

This copper derivative may be recrystallised by dissolving in boiling toluene, from which it separates as a green powder:

0.2220 gave 0.0300 CuO. Cu=10.8.

$(C_{12}H_{12}O_5N)_2Cu$ requires Cu=11.0 per cent.

The above copper compound was ground to a paste with water, mixed with powdered ice, and decomposed by shaking with dilute hydrochloric acid and ether. The ethereal solution was washed with water and then with aqueous sodium hydrogen carbonate, dried, and evaporated, when ethyl *o*-nitro-*p*-toluoylacetate was obtained in colourless plates, melting at 65–66°:

0.3577 gave 0.7511 CO_2 and 0.1614 H_2O . C=57.26; H=5.01.

0.3126 „ 15.4 c.c. N_2 at 20° and 754 mm. N=5.60.

$C_{12}H_{13}O_5N$ requires C=57.3; H=5.1; N=5.6 per cent.

The alcoholic solution gives an orange-red colour with ferric chloride. The crystals dissolve readily in dilute potassium hydroxide solution, forming a yellow solution. When concentrated potassium hydroxide solution is added to this solution there is precipitated the crystalline, yellow potassium derivative of ethyl *o*-nitro-*p*-toluoylacetate, $NO_2 \cdot C_6H_3Me \cdot CO \cdot CHK \cdot CO_2Et$:

0.2917 gave 0.0872 K_2SO_4 . K=13.4.

$C_{12}H_{12}O_5NK$ requires K=13.5 per cent.

o-Nitro-*p*-toluoylactic Acid.

Five grams of ethyl *o*-nitro-*p*-toluoylacetate were mixed with 10 c.c. of concentrated sulphuric acid, and the solution was kept at 80° for ten minutes. On cooling and adding ice, a white precipitate of *o*-nitro-*p*-toluoylactic acid was obtained, which was collected, dissolved in dilute sodium carbonate solution, and the filtered solution acidified with dilute hydrochloric acid. The precipitated acid was crystallised from warm benzene, when colourless needles were obtained, which melted and decomposed at 110°, carbon dioxide being evolved. It is readily soluble in alcohol or hot water, but almost insoluble in cold light petroleum. The alcoholic solution gives a deep red colour with ferric chloride:

0.2511 gave 0.4921 CO_2 and 0.0932 H_2O . C=53.5; H=4.1.

0.3020 „ 16.5 c.c. N_2 at 20° and 750 mm. N=6.2.

$C_{10}H_9O_5N$ requires C=53.8; H=4.0; N=6.3 per cent.

The acid, when boiled with water for five minutes, gave off carbon dioxide and left a yellow oil. This was extracted with ether, and proved to be *o*-nitro-*p*-tolyl methyl ketone.

It is very similar to *o*-nitroacetophenone. When heated with

zinc dust and soda-lime it gave a sublimate, which was evidently 6:6'-dimethylindigotin, thus behaving like *o*-nitroacetophenone, which in the same way gives indigotin.

6:6'-Dimethylindigotin.

o-Nitro-*p*-toluoylactic acid (10 grams) was dissolved in 100 c.c. of 10 per cent. sodium hydroxide solution. An indigo-blue precipitate appeared within ten minutes on keeping, and more rapidly when the solution was boiled. The yield of 6:6'-dimethylindigotin was not more than 50 per cent., and the addition of zinc dust to the alkaline solution improved the yield only a little.

6:6'-Dimethylindigotin crystallises from aniline in small plates with a coppery lustre, and very similar to indigotin. (Found: $N=9.44$. $C_{18}H_{14}O_2N_2$ requires $N=9.65$ per cent.) It may be sublimed under ordinary pressure with partial decomposition. It is very sparingly soluble in boiling alcohol with a blue colour; the solution in chloroform is reddish-blue, in nitrobenzene greenish-blue, and in paraffin wax violet.

Its properties are given in some detail by Kuhara and Chikashigé (*loc. cit.*).

Ethyl *p*-Toluylacetate.

The details for preparation are the same as described for ethyl *o*-nitro-*p*-toluylacetate. The quantities used for preparing *p*-toluoyl chloride were 100 grams of *p*-toluic acid and 155 grams of phosphorus pentachloride, and the reaction between the acid chloride (70 c.c.), ethyl acetoacetate (80 grams), and sodium ethoxide (20 grams of sodium in 480 c.c. of alcohol) was carried out in stages, as in the previous case. After hydrolysis with ammonia and ammonium chloride, the ethyl *p*-toluylacetate obtained (Found: $C=69.7$; $H=6.9$. $C_{12}H_{14}O_2$ requires $C=69.9$; $H=6.8$ per cent.) was purified through the copper compound (Found, $Cu=13.1$. Calc., $Cu=13.5$ per cent.).

On hydrolysis by warming at 80° for ten minutes with sulphuric acid, the ester gave *p*-toluylacetic acid (m. p. $98-100^\circ$; Found, $C=67.6$; $H=5.6$. Calc., $C=67.4$; $H=5.6$ per cent.), which, on being heated at its melting point or boiled with water, furnishes *p*-tolyl methyl ketone, boiling at $220^\circ/750$ mm. (oxime, m. p. 88°).

The author's thanks are due to the Research Fund Committee of the Chemical Society for a grant which has in part defrayed the cost of this investigation.

THE TECHNICAL COLLEGE,
HUDDERSFIELD.

CCIV.—*The Chemical Constitution of Dioximines.*

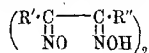
By LEO ALEXANDROVITSCH TSCHUGAEV.

SEVERAL years ago it was shown by the author that most of the metals belonging to the eighth group of the periodic systems form with the $\alpha\beta$ -dioximes (I) very characteristic complex compounds

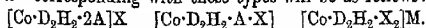


termed dioximines, and containing the general group II, in combination with the metallic atom. The dioximines are distinguished by their abnormal colour, and by a very high degree of stability, which is especially characteristic of the derivatives of platinum, palladium, nickel, cobalt, and rhodium (*Zeitsch. anorg. Chem.*, 1905, **46**, 144; *Ber.*, 1906, **39**, 2692; 1907, **40**, 3498; 1908, **41**, 1678, 2219, 2226; "On Complex Compounds," Moscow, 1906; Tschugaev and Lebedinski, *Zeitsch. anorg. Chem.*, 1913, **83**, 1). It may be pointed out that the two NO-groups, as well as the two NOH-groups making up the dioximino-complex above mentioned, are directly attached to the metallic atom, the two former exhibiting acid properties and the two latter showing the same behaviour as ammonia does in platammines or in cobaltammines. These conclusions, which may be deduced from a thorough examination of the properties and of the chemical behaviour of the cobaltidioximines, having been recently criticised by Mr. Atack (*T.*, 1913, **103**, 1317), I will summarise in this paper the chief arguments in favour of my views, partly based on experiments not yet published.

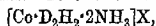
There are three types of the cobaltidioximines hitherto known. If we denote for brevity's sake the complex



as D_2H_2 (DH_2 meaning a molecule of an $\alpha\beta$ -dioxime), the general formulæ* corresponding with these types will be as follows:



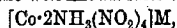
Now these compounds exhibit a very close analogy to a series of well-known cobaltammines. To take an instance, the salts,



of the complex base $[\text{Co}\cdot\text{D}_2\text{H}_2\cdot 2\text{NH}_3](\text{OH})$ are very similar to the croco-salts $[\text{Co}\cdot 4\text{NH}_3(\text{NO}_2)_2]\text{X}$; the salts of the complex acids

* In these formulæ X stands for a negative radicle (NO_2 , Cl, I, SCN), A for a molecule of NH_3 , NH_2R , etc., and M for a monad metallic atom (K, Na, etc.).

$[\text{Co} \cdot \text{D}_2\text{H}_2(\text{NO}_2)_2]\text{H}$, $[\text{Co} \cdot \text{D}_2\text{H}_2(\text{NO}_2) \cdot \text{CN}]\text{H}$, $[\text{Co} \cdot \text{D}_2\text{H}_2(\text{CN})_2]\text{H}$, etc., are quite analogous to the well-known salts of the series

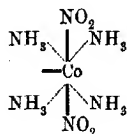


and the numerous representatives of the type $[\text{Co} \cdot \text{D}_2\text{H}_2 \cdot \text{A} \cdot \text{X}]$ ($\text{A} = \text{NH}_3$, Py , NH_2Et ; $\text{X} = \text{Cl}$, Br , I , NO_2 , SCN , N_3 , etc.) to the non-electrolytes $[\text{Co} \cdot 3\text{NH}_3(\text{NO}_2)_3]$.

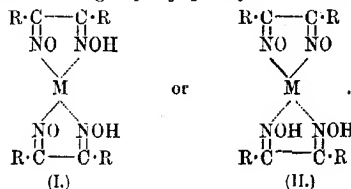
It will be seen at once from the comparison of the cobalt dioximines with the analogous cobaltammines that the complex radicle D_2H_2 everywhere stands for $2\text{NH}_3 \cdot \text{X}_2$, and that consequently two NOH -groups of this complex play the same part as 2NH_3 in metallammines.

Quite similar conclusions may be drawn from the study of the rhodidioximines, as has been shown recently by Lebedinski and the author (*loc. cit.*).

According to Werner's ("Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," 1913) well-known theory, which gives at the present state of our knowledge the most perfect record of the chemical behaviour and of the constitution of complex salts and of allied compounds, and affords a very valuable means for their classification, molecules like ammonia, amines, water, etc., in such compounds are to be considered as directly bound to the metallic atoms by means of auxiliary valencies. Thus we have for the ion of the croceo-salts:

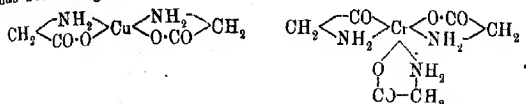


If we accept Werner's system we are led, therefore, to represent the constitution of the group $\text{D}_2\text{H}_2 \cdot \text{M}$ by one of the schemes:

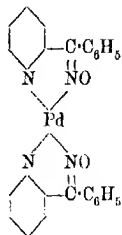


In the author's opinion formula I is the more probable one (although the other possibility is not excluded at all), first, because there is a very close analogy between the dioximines and numerous other representatives of the important class of the so-called inner complex salts, for instance, the copper, nickel, platinum, palladium, cobalt, and chromium salts of the α -amino-acids (*Ley, Zeitsch.*

Elektrochem., 1904, **10**, 954; "Konstitution und Farbe," 1911; Bruni and Fornara, *Atti R. Accad. Lincei*, 1904, [v], **13**, ii, 26; Tschugaev, *J. pr. Chem.*, 1907, [ii], **75**, 153; Tschugaev and Serbin, *Compt. rend.*, 1910, **151**, 1361) to which the following constitution has been assigned:



This analogy is greatly strengthened by the existence of inner complex salts derived from 2-benzoylpyridineoxime (Tschugaev, *Ber.*, 1906, **39**, 3382):

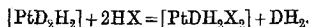


In this case the nitrogen atom of the pyridine molecule plays the same part as the oximino-group in the dioximes.

A further argument claimed in favour of formula II consists in that the two molecules of $\alpha\beta$ -dioxime which form the dioximine complex seemed to be almost inseparable. Until lately it was not possible to obtain a compound with but one molecule of $\alpha\beta$ -dioxime combined with a metallic atom, in striking contrast to the extreme facility with which the typical dioximes are formed.

Quite recently, however,* the author succeeded in preparing a series of such compounds corresponding with the formulæ $[\text{PtDH}_2\text{Cl}_2]$ and $[\text{PtDH}_2\text{Br}_2]$ by heating the platodioximes $[\text{PtD}_2\text{H}_2]$ with concentrated hydrochloric and hydrobromic acids. The chemical properties of these compounds having a direct bearing on Atack's criticism, their behaviour will therefore be discussed.

The formation of these compounds may be represented by the equation:

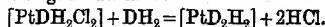


They are crystalline substances of a brownish-red colour, insoluble in water and sparingly soluble in chloroform, especially at its

* These experiments were carried out in the years 1911 and 1912 in conjunction with Mr. Onufriadi, Mr. Pentegov and Mr. Rumjanzev. The experimental part of this work will be published elsewhere.

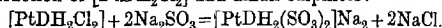
boiling point. They are very stable towards acids, but react readily with many other substances.

They react with one molecule of the α -dioxime DH_2 in neutral solutions, for example, on adding ammonium acetate or pyridine, regenerating the original dioxime:

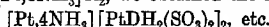


Ammonia also combines with them to form very soluble and almost colourless substances, which seem to be salts of a complex base, but their composition has not yet been established owing to the difficulty of obtaining them in the state of purity. It is to be noticed that the dichloro-derivative $[\text{PtDH}_2\text{Cl}_2]$ is not precipitated from the ammoniacal solution on addition of hydrochloric acid in the cold, but it is readily formed on heating the mixture.

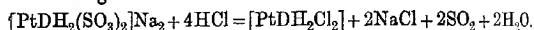
On the other hand, we succeeded in obtaining salts of the dibasic acid, $[\text{PtDH}_2(\text{SO}_3)_2]\text{H}_2$, corresponding with dimethylglyoxime by the interaction of $[\text{PtDH}_2\text{Cl}_2]$ and alkali sulphites:



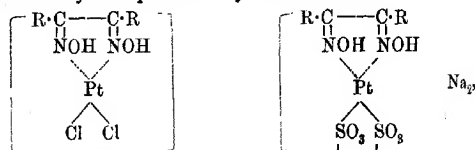
The sodium salt is a pink-coloured, crystalline substance, readily soluble in water. By reaction with guanidine hydrochloride the characteristic, comparatively sparingly soluble guanidine salt, $[\text{PtDH}_2(\text{SO}_3)_2]\text{C}(\text{NH}_2)_2 \cdot \text{NH}_4\text{H}$, is formed. With the chloride of the I. Reiset's base, $[\text{Pt}_4\text{NH}_3]\text{Cl}_2$, we obtained the salt



From solutions of this salt the compound $[\text{PtDH}_2\text{Cl}_2]$ is precipitated by acids (hydrochloric acid, etc.) only on heating, sulphur dioxide being evolved:



It appears, therefore, very probable that the constitution of these compounds may be represented by the formulæ:

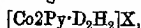


the group DH_2 exhibiting the same function as the molecule of ethylenediamine (en) in $[\text{Pt en Cl}_2]_2$, and occupying two co-ordination places.

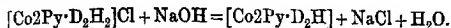
It appears from these facts that both oximino-groups of $\alpha\beta$ -dioximes taking part in the formation of complex compounds may display a basic as well as an acidic function.*

* This conclusion being drawn from experimental facts concerning the aliphatic dioximes, experiments are now in progress with a view to ascertain if the same is true in the aromatic series also.

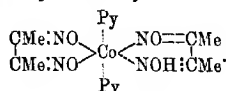
This conclusion is supported by the following facts established by Mr. Postnikov and myself some years ago. It was pointed out that the complex base $[\text{Co}2\text{Py}\cdot\text{D}_2\text{H}_2]\text{OH}$ (Py=pyridine, DH_2 =dimethylglyoxime), corresponding with the series of salts



is very unstable, and loses 1 molecule of water at the same time as it is set free on addition of sodium hydroxide to a solution of one of its salts:



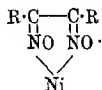
Now it is obvious that in the resulting "anhydro-base," $[\text{Co}2\text{Py}\cdot\text{D}_2\text{H}]$, three of the four oximino-groups exhibit acidic functions, as may be represented by the formula:



We may now consider the characteristic behaviour of isomeric β -dioximines towards metallic salts. As it was pointed out by the author, it is only the *syn*-modifications that are capable of giving typical dioximines with nickel, cobalt, palladium, platinum, iron, and copper salts, whereas the *anti*- and *amphi*-modifications do not possess this property. If we assume the Hantzsch-Werner's stereochemical hypothesis, it may be concluded from these facts that the possibility of dioximines being formed may exist only in the case of a peculiar spacial configuration suitable for ring-formation.

On the other hand, the differences existing between the *syn*-dioximines and the other isomeric forms (*anti* and *amphi*) allow us to distinguish these isomeric forms from each other by means of very simple qualitative tests.

Now Atack observed a further difference of a more delicate character between the *anti*- and *amphi*-modifications, the former being wholly incapable of forming nickel salts, whereas from the *amphi*-modification such salts may be obtained. In these salts, however, the nickel atom is combined with one molecule of the dioxime only, both the NOH-groups exhibiting acidic properties, as is seen from the formula:



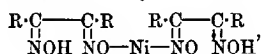
Moreover, these salts are not so stable as the typical dioximines, especially towards acids.

It may here be remarked that Atack is incorrect in attributing to me the opinion that the γ -(*amphi*)dioximes are wholly incapable

of giving nickel salts. All I assert with regard to this is stated in the following passage from my paper, cited by Atack himself: "Die Fähigkeit zur Bildung der charakteristischen *Dioxime* kommt nur den syn-Modifikationen, nicht dagegen den anti- und anti-Modifikationen der 1:2-Dioxime zu."

It is well known that the capacity of forming salts is a general property of oximes, and it was ascertained by the author that the salts of certain heavy metals are generally distinguished by a somewhat higher degree of stability than those derived from alkali metals. The yellow nickel salts of the *amphi-αβ*-dioximes obtained by Atack belong probably to this category of metallic salts, their stability being still more increased by the ring-formation, but, notwithstanding, they are not to be considered as typical dioximes, for they possess quite a different composition and a different chemical function.

As to the constitution of the dioximes the experimental results obtained by Atack, in the author's opinion, are by no means in opposition to the formulæ hitherto accepted for these compounds. On the contrary, if we assume with Atack that each molecule of an *αβ*-dioxime taking part in the formation of the complex molecule is attached to the metallic atom by means of one NO-group only:



the chief features of the chemical character of the dioximes remain altogether inexplicable, namely:

(1) The striking analogy of the cobalti- and rhodi-dioximes to the corresponding cobalti-ammines and rhodi-ammines above mentioned.

(2) The fact that the dioximes are altogether incapable of reacting with phenylcarbylamine. The NOH-groups within the complex molecule cannot consequently be considered as being in the free (uncombined) state.

(3) The exceptionally high degree of stability of the dioximes, which renders quite improbable the assumption that the NOH-groups do not participate in the formation of the complex molecule.

(4) The close analogy, already alluded to, existing between dioximes and other inner complex salts.

(5) The fact that the capacity of forming typical dioximes is confined to the *αβ*-dioximes, the *αγ*- and *αε*-dioximes being without this property.

As was pointed out by the present author, all these peculiarities of the complex dioximes can be easily explained by the cyclic constitution of their molecule.

Atack concluded from his experiments that in *αβ*-dioximes one

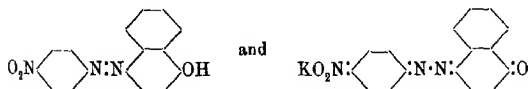
NOH-group is basic and the other acidic. As we have seen, the facts recorded in this paper suggest, on the contrary, that these groups, at least in the aliphatic series, may, in different cases, exert basic as well as acidic properties. Even on the assumption that Attack's opinion is well founded, it appears improbable from the data at present available that the basic variety of the oximino-group should not participate at all in the formation of the complex molecule.

THE UNIVERSITY,
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CCV.—Colour and Constitution of Azo-compounds. Part VI.

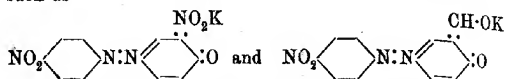
By JOHN THEODORE HEWITT, GLADYS RUBY MANN, and
FRANK GEORGE POPE.

SOME years ago one of the authors of this communication suggested (Hewitt and Mitchell, T., 1906, 89, 19) that whilst the hydroxyazo-compounds and their salts are generally of the same type, the hydrogen of the hydroxyl group being simply replaced by metal, a change of molecular structure occurred when a metallic salt was produced by the action of a base on an azo-compound containing both a hydroxyl and a nitro-group situated in different nuclei and each in the para-position with respect to the azo-group, for example, *p*-nitrobenzeneazo- α -naphthol and its potassium salt have structures which may be represented by the formulae



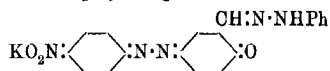
The question was fully discussed by Hewitt and Mitchell in a later paper (T., 1907, 91, 1251), new experimental evidence being brought forward in support of the view expressed, and several observations of other chemists correlated. Attention was particularly directed to Meldola's observation that whilst most *p*-hydroxy-azo-compounds undergo fission on reduction, whether in acid or alkaline solution, *p*-nitrobenzeneazophenol and similarly constituted compounds may be reduced in alkaline solution by ammonium sulphide, with the formation of the corresponding *p*-amino-*p*'-hydroxyazo-compounds (T., 1885, 47, 659).

The very marked shift in the absorption which accompanies the conversion of *p*-nitrobenzeneazophenol into an alkaline salt is not observed when an extra nitro-group or an aldehyde residue is introduced into the molecule in the ortho-position with respect to the hydroxyl group, the explanation offered in this case being that *o*-quinonoid structure is set up, the salts formed possessing structures such as



It will be noticed that there is no longer the possibility of both nuclei assuming a para-quinonoid configuration.

Support for this view in the case of the derivatives of salicylaldehyde is afforded by the work of Hantzsch (*Ber.*, 1906, 39, 3080), and in the special case of *p*-nitrobenzeneazosalicylaldehyde, Hewitt and Mitchell (*loc. cit.*, p. 1257) saw strong confirmation of their views in the fact that whilst the alcoholic and alkaline solutions of this compound are both yellow, the corresponding phenylhydrazone dissolves in organic solvents with a yellow colour, but with a bluish-purple shade in alcoholic potassium hydroxide. The oxygen of the $\cdot\text{CHO}$ group having been replaced by $\cdot\text{N}\cdot\text{NHPh}$, salt-formation with *o*-quinonoid structure is prevented, and the nitro-group comes into play, the potassium salt having the structure



An interesting point arose in connexion with the alteration of structure on salt-formation. If the group $\cdot\text{COR}$ ($\text{R}=\text{H}$ or alkyl) takes part in salt-formation when ortho to the hydroxyl group, it might be expected to play a part also when introduced into an azo-phenol in the para-position with respect to the azo-grouping, and one of the present authors, soon after the appearance of Hewitt and Mitchell's paper, instituted experiments bearing on this question. It was found that the product obtained by coupling diazotised *p*-aminobenzophenone with α -naphthol gave reddish-brown solutions in alcohol, but on addition of alkali the colour changed to a deep purple.

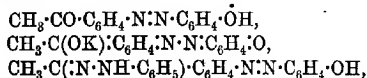
The work was not completed at the time, but in discussing the matter with Professor A. G. Green, one of the authors was informed that *p*-aldehydeazophenolic compounds underwent a similar marked colour change.

The work has now been resumed, and *p*-aminoacetophenone and *p*-aminobenzophenone have been diazotised and coupled in each case with phenol, *p*-cresol, and α - and β -naphthols. In every case

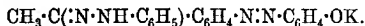
the addition of alkali to the alcoholic solution has resulted in a marked shift of the absorption towards the red end of the spectrum.

It has been noted above that whilst *p*-nitrobenzeneazosalicylaldehyde gives yellow alkaline solutions, addition of alkali to the alcoholic solution of the corresponding phenylhydrazone develops a purple colour. If our view is correct, then the effect of alkali on the phenylhydrazone of a *p*-ketobenzeneazophenol should be less marked than on the parent ketone, and a reference to Fig. 1 will show that this expectation has been fulfilled. The head of the band for *p*-acetylbenzeneazophenol lies at an oscillation frequency of 2750 in alcoholic solution, whilst on rendering alkaline the head is shifted to 2100. Conversion of the *p*-acetylbenzeneazophenol into its phenylhydrazone is accompanied by a broadening of the band and shifting of its head from 2750 to 2450, but when the solution of this phenylhydrazone is rendered alkaline, the head of the band is shifted only to 2300.

Thus it is seen that whilst the band for the phenylhydrazone lies on the red side of that for the ketone, the positions are reversed in the case of the alkaline salts. This result appears to be in accord with the view that the compounds and their salts have the constitutions



and



That a considerable displacement of the absorption also takes place when alkali is added to any of the *p*-ketobenzeneazophenols is apparent from the figures; it is only in the case of *p*-acetylbenzeneazophenol that the absorption spectra of the phenylhydrazone and its alkaline salt have been measured. The preparation of phenylhydrazones of ketones of the types described in the present paper presents considerable difficulty, and in some cases repeated attempts to bring phenylhydrazine into reaction with the azoketones ended in failure.

EXPERIMENTAL.

β-Acetylbenzeneazophenol, $\text{CH}_3\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$.

This compound was prepared by diazotisation of *p*-aminoacetophenone and coupling with phenol. It separates from dilute alcohol in orange-red plates, which melt at 196° (uncorr.*):

* The melting points recorded in this paper are uncorrected for the exposed stem of the thermometer.

0.1336 gave 0.3434 CO_2 and 0.0574 H_2O . $\text{C}=70.1$; $\text{H}=4.78$.

0.1496 „ 15.1 c.c. N_2 at 18° and 746.6 mm. $\text{N}=11.43$.

$\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_2$ requires $\text{C}=70.0$; $\text{H}=5.0$; $\text{N}=11.67$ per cent.

Addition of alkali to the brown alcoholic solution of the azo-phenol develops a purple shade.

The *acetyl* derivative separates from glacial acetic acid in small, brownish-red prisms, which melt at 130° :

0.1784 gave 15.4 c.c. N_2 at 18° and 764 mm. $\text{N}=10.07$.

$\text{C}_{16}\text{H}_{14}\text{O}_3\text{N}_2$ requires $\text{N}=9.93$ per cent.

The *benzoyl* derivative was prepared by dissolving the azophenol in pyridine and adding the calculated amount of benzoyl chloride to the solution. It forms small, scarlet prisms, which melt at 210° :

0.2120 gave 15.3 c.c. N_2 at 23.5° and 764.6 mm. $\text{N}=8.18$.

$\text{C}_{21}\text{H}_{16}\text{O}_3\text{N}_2$ requires $\text{N}=8.14$ per cent.

The *phenylhydrazone*, $\text{CH}_3\cdot\text{C}(\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_5)\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, is obtained by mixing hot alcoholic solutions of the azophenol and of phenylhydrazine. The mixture was allowed to remain overnight, the precipitate collected, washed, and crystallised from dilute alcohol. It separated in small, brownish-yellow needles, melting at 194° :

0.1014 gave 14.8 c.c. N_2 at 17° and 767.4 mm. $\text{N}=17.28$.

$\text{C}_{20}\text{H}_{18}\text{ON}_4$ requires $\text{N}=16.97$ per cent.

The curves in Fig. 1 give the absorption spectra of the azophenol and its phenylhydrazone in alcoholic solution, as well as the spectra observed when an excess of alkali is added to the alcoholic solutions. The much greater displacement of the absorption on rendering a solution of the azophenol alkaline than is the case with the phenylhydrazone has been remarked on in the introduction.

p-Benzoylbenzeneazophenol, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, obtained from diazotised *p*-aminobenzophenone and phenol, separates from dilute alcohol in small, orange-red needles, which melt at 157° :

0.1802 gave 15.2 c.c. N_2 at 19° and 745.7 mm. $\text{N}=9.57$.

$\text{C}_{19}\text{H}_{14}\text{O}_2\text{N}_2$ requires $\text{N}=9.27$ per cent.

The *acetyl* derivative crystallises from glacial acetic acid in brownish-red plates, which melt at 159° :

0.2063 gave 14.7 c.c. N_2 at 23° and 767 mm. $\text{N}=8.21$.

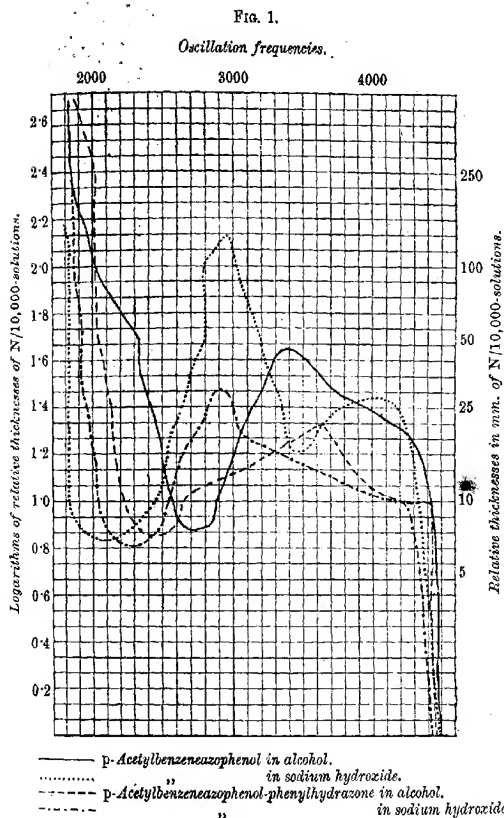
$\text{C}_{21}\text{H}_{16}\text{O}_3\text{N}_2$ requires $\text{N}=8.14$ per cent.

The *benzoyl* derivative was obtained by benzoylation in pyridine solution (2 grams of the azo-phenol, 40 c.c. of pyridine, 1.5 grams of benzoyl chloride); it separates from glacial acetic acid in orange-red needles, which melt at 162° :

0.1600 gave 9.8 c.c. N_2 at 19° and 749 mm. $N=6.93$.

$C_{20}H_{18}O_3N_2$ requires $N=6.90$ per cent.

Fig. 2 shows the absorption spectra of *p*-benzoylbenzeneazophenol in alcoholic solution, both without and with the addition of alkali.



It will be noticed that the heads of the absorption bands occur at much the same oscillation frequencies as in the case of *p*-acetylbenzeneazophenol.

p-Acetylbenzeneazo-*p*-cresol, $CH_3 \cdot CO \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(CH_3) \cdot OH$,
VOL. CV. 7 D

crystallises from alcohol in small, brownish-red needles, which melt at 122° :

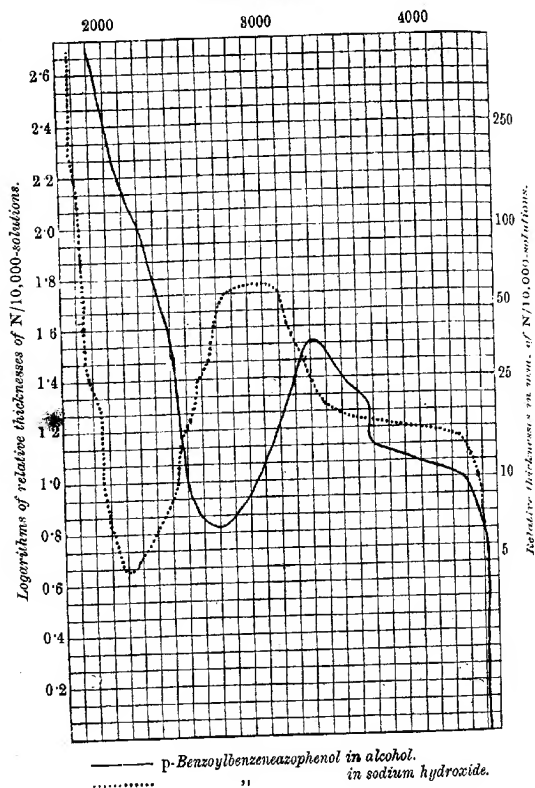
0.0888 gave 0.2309 CO_2 and 0.0418 H_2O . $\text{C}=70.91$; $\text{H}=5.25$.

0.1158 " 11.1 c.c. N_2 at 15.5° and 754.8 mm. $\text{N}=11.09$.

$\text{C}_{15}\text{H}_{14}\text{O}_2\text{N}_2$ requires $\text{C}=70.89$; $\text{H}=5.51$; $\text{N}=11.02$ per cent.

FIG. 2.

Oscillation frequencies.



The *acetyl* derivative, as obtained in the ordinary manner crystallises from dilute alcohol in small, brown needles, melting at 104° :

0.1756 gave 14.4 c.c. N_2 at 21° and 766.4 mm. $N=9.5$.

$C_{17}H_{16}O_2N_2$ requires $N=9.43$ per cent.

The *benzoyl* derivative, prepared by the Schotten-Baumann method, separates from dilute alcohol in brown needles, which melt at 139° :

0.155 gave 10.8 c.c. N_2 at 17° and 769.5 mm. $N=8.01$.

$C_{22}H_{18}O_3N_2$ requires $N=7.83$ per cent.

The *phenylhydrazone* was prepared by mixing equivalent quantities of the azo-cresol and phenylhydrazine in glacial acetic acid. The mixture was allowed to remain for three days, and the precipitate, after collection and washing, recrystallised several times from glacial acetic acid. It separates in small, dark maroon-coloured needles, exhibiting a slight bronze reflex, and melting at 156° :

0.1434 gave 20.8 c.c. N_2 at 25° and 757.4 mm. $N=16.66$.

$C_{21}H_{20}ON_4$ requires $N=16.28$ per cent.

The colour of the alcoholic solution is deepened by the addition of alkali, but the change is much less marked than in the case of the parent ketonic azophenol.

p-Benzoylbenzeneazo-p-cresol, $C_6H_5 \cdot CO \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(CH_3) \cdot OH$, separates from alcohol in small, golden-yellow needles, which melt at 148° :

0.1665 gave 13.0 c.c. N_2 at 14° and 743.4 mm. $N=8.93$.

$C_{20}H_{16}O_2N_2$ requires $N=8.86$ per cent.

The *acetyl* derivative separates from alcohol in brownish-red needles, melting at 94° :

0.2640 gave 18.0 c.c. N_2 at 20° and 765.4 mm. $N=7.92$.

$C_{22}H_{18}O_3N_2$ requires $N=7.82$ per cent.

The *benzoyl* derivative, prepared by the usual Schotten-Baumann method, crystallised from glacial acetic acid in orange-red needles, which melted at 151° :

0.1878 gave 10.4 c.c. N_2 at 17° and 766.7 mm. $N=6.56$.

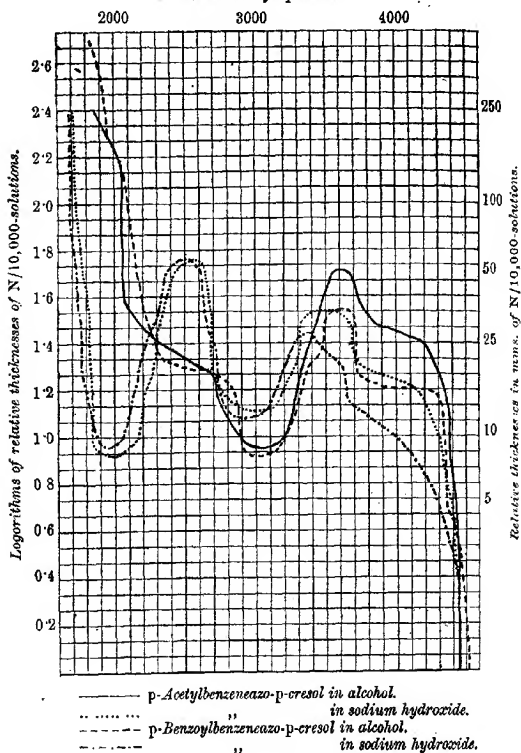
$C_{27}H_{20}O_3N_2$ requires $N=6.67$ per cent.

Fig. 3 gives the absorption curves of the two ketobenzeneazo-*p*-cresols, as well as of their alkali salts. Attention may be drawn to the great similarity of the absorption shown in each case, and the small effect produced by replacing alkyl by aryl in the ketonic coupling. Conversion of the azo-phenol into an alkaline salt is accompanied by a much greater displacement in the case of these hydroxyazo-compounds than is observed in the *p*-series (compare g. 1).

p-Acetylbenzeneazo- α -naphthol, $CH_3 \cdot CO \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot OH$, was

prepared by coupling diazotised *p*-aminoacetophenone with α -naphthol dissolved in 96 per cent. alcohol. On mixing the two solutions, the whole sets to a crystalline paste of the hydrochloride of the azonaphthol. This was collected, washed, dissolved in sodium hydroxide solution, and the azo-compound precipitated by the addi-

FIG. 3.
Oscillation frequencies.



tion of acetic acid. The compound separates from nitrobenzene in small, dark red needles, which melt and decompose at 248–249°.

0.1035 gave 0.2799 CO₂ and 0.0448 H₂O. C=73.75; H=4.81.

0.1762 " 14.6 c.c. N₂ at 18° and 756.5 mm. N=9.57.

C₁₈H₁₄O₂N₂ requires C=74.45; H=4.83; N=9.66 per cent.

The alcoholic solution is deep red; addition of alkali changes the colour to an intense purple.

The *acetyl* derivative separates from glacial acetic acid in orange needles, melting at 141° :

0.0804 gave 5.4 c.c. N_2 at 19° and 767.8 mm. $N = 8.43$.

$C_{20}H_{16}O_2N_2$ requires $N = 8.44$ per cent.

The *benzoyl* derivative prepared by the Schotten-Baumann method forms small, dark red needles, melting at 214° :

0.2634 gave 16 c.c. N_2 at 22° and 766.5 mm. $N = 7.06$.

$C_{25}H_{18}O_3N_2$ requires $N = 7.11$ per cent.

p-Benzoylbenzeneazo- α -naphthol, $C_6H_5 \cdot CO \cdot C_6H_4 \cdot N=N \cdot C_{10}H_7 \cdot OH$, crystallises from glacial acetic acid in very small, brownish-red needles, melting and decomposing at 241° :

0.1241 gave 0.3570 CO_2 and 0.0500 H_2O . $C = 78.48$; $H = 4.49$.

0.1780 " 12.6 c.c. N_2 at 17° and 744.5 mm. $N = 8.07$.

$C_{23}H_{18}O_2N_2$ requires $C = 78.42$; $H = 4.55$; $N = 7.96$ per cent.

A similar colour change is observed as with the preceding azo-naphthol when the alcoholic solution is rendered alkaline.

The *acetyl* derivative crystallises from dilute alcohol in brown needles, melting at 140° :

0.2378 gave 14.7 c.c. N_2 at 19° and 765.4 mm. $N = 7.22$.

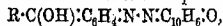
$C_{25}H_{18}O_3N_2$ requires $N = 7.11$ per cent.

The *benzoyl* derivative was prepared by benzoylation in pyridine solution, and separated from glacial acetic acid in felted, orange needles, which melt at 164° :

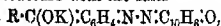
0.2084 gave 10.6 c.c. N_2 at 17° and 766.4 mm. $N = 5.97$.

$C_{30}H_{20}O_3N_2$ requires $N = 6.14$ per cent.

The absorption curves of alcoholic solutions of *p*-acetyl- and benzoyl-benzeneazo- α -naphthols are shown in Fig. 4. It will be again noted that replacement of methyl by phenyl in the ketonic group produces very little change in the character of the absorption; more remarkable is the comparatively slight shift produced in each case when the solutions are rendered alkaline. It would be unwise to conclude without further evidence that these azo-naphthols exist in alcoholic solution in a quinonoid form,



corresponding in structure with the salts



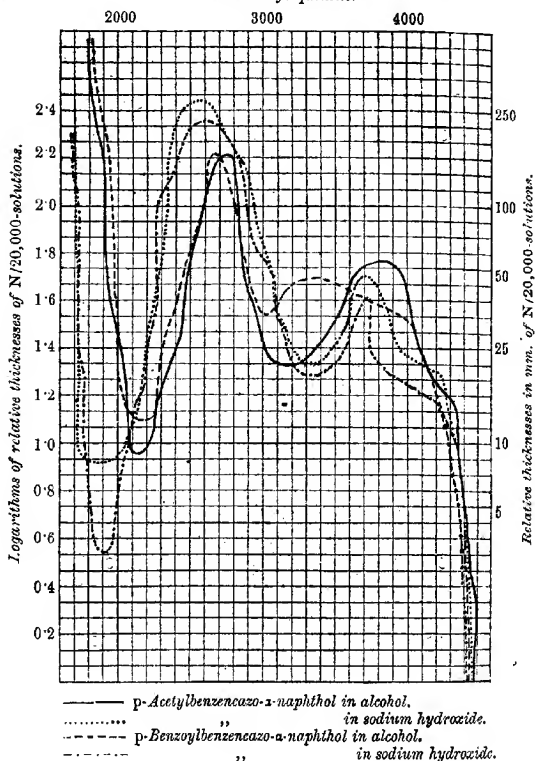
but it is at least significant that these compounds show little, if any, tendency to react with phenylhydrazine.

In Fig. 5 the curves are shown for the corresponding derivatives of β -naphthol, and it is again noticeable that the change from methyl to phenyl has very little effect on the absorption. Addition

of alkali to the alcoholic solutions produces only a slight shift of the absorption to the red end of the spectrum; the phenylhydrazone of *p*-acetylbenzeneazo- β -naphthol is, however, formed with comparative ease.

p-Acetylbenzeneazo- β -naphthol, $\text{CH}_3\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$,

FIG. 4.
Oscillation frequencies.



crystallises from nitrobenzene in small, scarlet needles, melting at 183° :

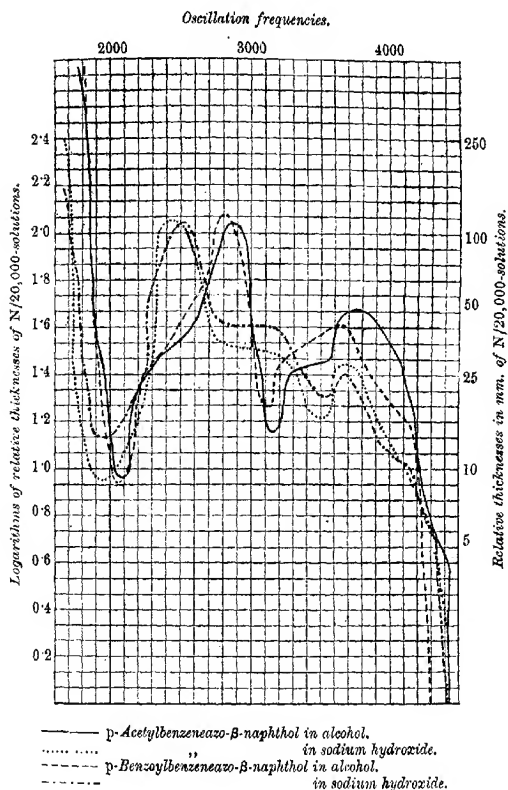
0.1074 gave 0.2844 CO_2 and 0.0476 H_2O . $\text{C}=74.10$; $\text{H}=5.04$.

0.1626 " 13.3 c.c. N_2 at 16° and 761.4 mm. $\text{N}=9.58$.

$\text{C}_{18}\text{H}_{14}\text{O}_2\text{N}_2$ requires $\text{C}=74.45$; $\text{H}=4.83$; $\text{N}=9.66$ per cent.

The *phenylhydrazone* was obtained on mixing glacial acetic acid solutions of 2 grams of the azo-compound and 1 gram of phenylhydrazine. The whole set to a mass of very dark, glistening crystals, which were collected, washed with small quantities of

FIG. 5.



acetic acid, and then crystallised from the same solvent. The compound melts at 201°:

0.1238 gave 15.65 c.c. N_2 at 21° and 756.5 mm. $N = 14.5$.

$C_{24}H_{20}ON_4$ requires $N = 14.74$ per cent.

p-Benzoylbenzeneazo- β -naphthol, $C_6H_5 \cdot CO \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot OH$, crystallises from glacial acetic acid in scarlet needles, melting at 189° :

0.1866 gave 13.1 c.c. at 14° and 747.2 mm. $N=8.12$.

$C_{23}H_{16}O_2N_2$ requires $N=7.96$ per cent.

It was found impossible either to acetylate or benzoylate this compound; the great resistance of some of the azo-derivatives of β -naphthol to acylation is already well known.

In conclusion, we desire to tender our thanks to the Research Fund Committee of the East London College for a grant defraying the cost of this investigation.

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CCVL.—*The Volumetric Estimation of Carbon in Aliphatic Substances in the Wet Way.*

By EGERTON CHARLES GREY (Beit Memorial Research Fellow).

THE original method of estimating carbon in the wet way by heating the substance with potassium dichromate and sulphuric acid or with chromic acid, with which the names of Rogers, Brunner Ullgrens, and Classen are associated, is described by Fresenius ("Anleitung zur quantitativen Chemische Analyse"). The substance was at first heated with the chromic acid mixture in a stream of air, but later Classen introduced a reflux condenser, whereby the distillation of water was prevented, and also traces of volatile chromium compounds. The method has been chiefly employed in the analysis of soils (Wolff, "Anleitung zur chemischen Untersuchung landwirtschaftlich wichtiger Stoffe"), and for carbon in steel and iron (Blair, *J. Amer. Chem. Soc.*, 1896, 18, 223). In the case of soils, however, the method gave low results (Warrington and Peak, T., 1880, 37, 617, and Cameron and Breazeale, *J. Amer. Chem. Soc.*, 1903, 26, 29), which have been variously attributed to the formation of carbon monoxide, acetaldehyde, acetic acid, and other substances not completely oxidised.

It has been most generally assumed that low results are due to

carbon monoxide, but although under certain conditions this gas may be formed, its production can certainly be avoided in the case of aliphatic substances by using a proper excess of oxidising agent. On the other hand, it is more likely that the low results observed by many workers were due to acetic acid, which substance is attacked only with great difficulty by the chromic acid mixture.

In the present communication a method is described for the estimation of the total carbon in aliphatic substances, which depends on the gasometric measurement of carbon dioxide, followed by the determination of the acetic acid in the residual fluid, and it is shown that the method gives accurate results.

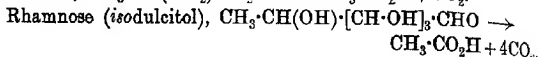
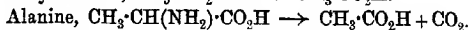
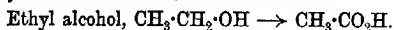
The apparatus employed is very similar to that already described by Blair, but mercury is used in the place of the salt solution employed by that author. This form of apparatus, in which the solution of the substance is allowed to boil in contact with the oxidising agent until completely oxidised either to carbon dioxide or to a mixture of carbon dioxide and acetic acid, is clearly better in principle than the method in which the products are allowed to escape from the sphere of the reaction in a partly oxidised condition.

Messinger (*Ber.*, 1890, **23**, 2756) overcame the difficulty of incomplete oxidation by allowing the vapours from the chromic acid mixture to pass through a combustion tube containing red-hot copper oxide, and lead chromate and potassium dichromate have also been employed in the same way (Hall, Miller, and Marmu, *T.*, 1906, **89**, 595), but the introduction of these modifications deprives the method of all its original simplicity.

The author has devoted his attention to this method chiefly with the object of applying it to the estimation of substances of biological importance, such as the alcohols and amino-acids, for which accurate methods are not available. The estimation of acetic acid, as well as of carbon dioxide, makes the method of general application to all aliphatic substances which are likely to occur in biological fluids, and the method has a further valuable application in the accurate estimation of alcohol and other volatile substances in dilute solutions.

The method has a great advantage in that it throws light on the constitution of the substance at the same time as it determines the percentage of carbon, for the titre of the acetic acid indicates the number of methyl groups in the compound; thus ethyl alcohol is oxidised practically quantitatively to acetic acid; propionic acid, and its derivatives, lactic acid and alanine, yield acetic acid corresponding with two carbon atoms out of three, whereas rhamnose yields two atoms of carbon out of the six in the form of acetic

acid. In each case the methyl group, together with the next adjacent carbon atom, forms acetic acid.



A small amount of acetic acid is at the same time oxidised to carbon dioxide, so that the value for the latter is greater than would theoretically be the case if the whole of the methyl group, together with the next adjacent carbon atom, were converted into acetic acid. The excess of carbon dioxide formed in this way is greatest when the oxidising fluid contains least water.

In the place of chromic acid, which, it seems, is always used with phosphoric acid, potassium dichromate has been used in this work. It has many advantages over chromic acid apart from its being free from impurities, since it may be weighed out and introduced into the flask much more conveniently than chromic acid. Moreover, only by using potassium dichromate, and avoiding the dilution of the oxidising medium by water, has it been found possible to effect the complete oxidation of carbamide.

It should be noted that the weight of material used for the analysis in many cases is considerably less than that generally employed for a dry combustion, and the method is certainly readily adaptable to microchemical analysis.

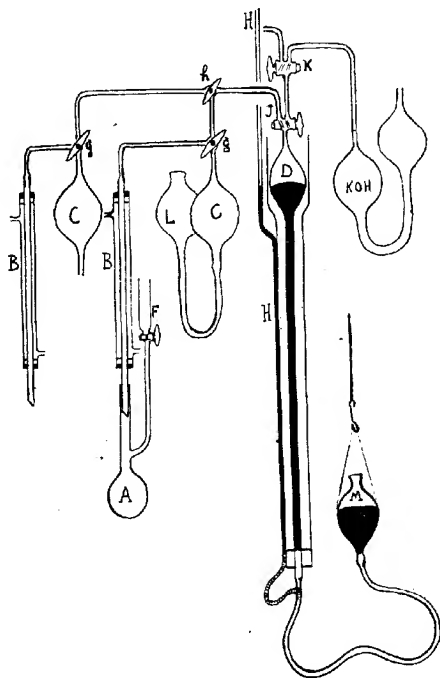
With most substances the oxidation is complete in from fifteen to thirty minutes, but others, such as carbamide and succinic acid, require longer, it being necessary to continue the heating for three hours. The operation requires, however, only a few minutes' actual attention, and two flasks with reflux condensers may be quite conveniently attached to the one gas analysis apparatus, so that two analyses may be carried out concurrently.

EXPERIMENTAL.

The apparatus employed is figured below. The gases are collected in the reservoirs rather than directly in the gas-measuring burette for several reasons. It will suffice to mention that in this way two flasks may be used in conjunction with the one burette, and, moreover, the burette itself is kept free from any traces of chromate which occasionally, although rarely, pass into the gas-collecting apparatus when the gases are swept out of the flask with the hot water.

Details of the Manipulation.—Fifteen grams of potassium dichromate are introduced into the flask A, which has a capacity

of about 75 c.c., and to this is added 15 c.c. of phosphoric acid (D 1.75). The flask is then attached to the reflux condenser *B* (internal tube 30×1 cm.), which is in communication through a capillary tube with the reservoir *C*. The tap of the funnel *F*, after having been smeared with phosphoric acid, is closed, and heat is applied to the flask *A*, the three-way tap *g* being turned so as to put *C* in communication with *B*, the vessel *L* being at the same



time lowered. About 4 c.c. of the fluid to be examined is now introduced into the funnel *F* (it is most convenient to weigh out the fluid from a bent pipette), and as soon as the potassium dichromate has mostly dissolved, and the chromic acid been set free, the solution is gradually allowed to be drawn into *A*. The funnel is then washed out into the flask with a few c.c. of water, followed by phosphoric acid, which is added to prevent the dilution of the oxidising fluid.

The heating is now continued for about thirty minutes, unless carbamide or succinic acid is present, when three hours is necessary. At the end of this time the flame is removed, the water allowed to run out of the condenser, and the residual gases in the flask are displaced by introducing hot water which has been boiled to remove carbon dioxide, into the flask *A*, through the funnel *F*, a lower pressure having been created within the flask by lowering the vessel *L*. The tap *g* is closed as soon as the hot water is seen in the capillary connecting *B* and *C*. The sample of gas may now be drawn into the measuring burette by lowering *M* and opening *J*. The adjustment to atmospheric pressure is made approximately by levelling with the mercury manometer tube *H*, and the fine adjustment is made by putting the gas into connexion with the potassium hydroxide of the Hempel bulbs. The measurement of the carbon dioxide is then carried out in the ordinary way.

When methyl groups may be present in the substance to be examined, the fluid, including that in the inner tube of the reflux condenser, is transferred when cold to a distilling apparatus, and distilled in steam in an atmosphere free from carbon dioxide.

The distillation in steam requires special precautions. The steam is generated by boiling distilled water treated with baryta, and to prevent minute traces of phosphoric acid being carried over into the distillate, the steam, after passing through the boiling acid solution, is made to pass through a second flask before being condensed. The lower tube of the condenser passes through a doubly bored rubber stopper into the neck of a large separating funnel, which acts as a receiver for the condensing fluid, and is protected from the access of atmospheric carbon dioxide by means of a soda-lime tube connected to a glass tube passing through the second hole of the rubber stopper. In this way, when fluid is withdrawn from the funnel, air free from carbon dioxide takes its place.

The results obtained with certain representative aliphatic substances are given below. Results with fatty acids of high molecular weight will be reserved for a later communication.

It must be mentioned that the phosphoric acid employed contained organic impurity, so that an allowance of from 1.5 to 2.6 c.c. of carbon dioxide had to be made in each experiment, according to the length of heating. Inasmuch as the amount of carbon dioxide produced from the phosphoric acid varies with the time of heating, it is of advantage previously to heat the phosphoric acid with a little chromic acid for some hours under a reflux condenser. A large amount of phosphoric acid may be readily

treated in this way, and its use is of advantage, especially when working with very small amounts of material.

Substance.	Weight taken.	Moist CO ₂ .	Temp.	Press.	Baryta N/30.	Carbon found.			Theoryt
						As acetic acid.	As CO ₂ .	Total.	
Sucrose ...	0.0353	30.1	20.0	765	—	—	42.13	42.13	42.11
" ...	0.0745	65.2	26.0	769	—	—	42.17	42.17	
" ...	0.0657	56.8	23.5	771	—	—	42.35	42.35	
Glycerol ...	0.0902	79.65	23.5	763	—	—	38.86	38.86	39.13
" ...	0.0488	39.31	23.2	761	—	—	38.97	38.97	
Mannitol...	0.0426	33.00	15.0	762	—	—	39.16	39.16	39.56
Uric acid.	0.0160	11.30	15.0	757	—	—	35.35	35.35	35.71
Carbamide	0.0782	31.96	21.6	764	—	—	20.01	20.01	20.00
Succinic acid	0.0191	15.70	22.5	787	—	—	40.23	40.23	40.66
Cystine ...	0.0270	15.18	24.0	761	—	—	30.30	30.30	30.00
Ethyl alcohol..	0.09638	2.3	23.3	754	61.27	50.87	1.16	52.03	52.17
Propionic acid.....	0.07424	36.0	28.0	765	23.31	23.02	25.13	48.15	48.65
Lactic acid	0.0714	25.53	26.0	766	20.40	17.37	22.85	40.22	40.00
Alanine ...	0.0733	18.54	23.0	761	22.82	12.26	27.78	40.04	40.44
"	0.1097	31.98	25.3	770	36.36	14.12	26.52	40.64	
Rhamnose	0.1170	66.95	27.0	769	17.32	27.43	11.84	39.27	39.55
"	0.1265	72.00	26.0	769	18.78	27.42	11.88	39.30	

General Conclusions.

Aliphatic substances can, in general, be oxidised to carbon dioxide, or to a mixture of carbon dioxide and acetic acid, by using potassium dichromate and phosphoric acid.

A volumetric method is described for the estimation of total carbon which is based on the estimation of these two products, the carbon dioxide being determined gasometrically and the acetic acid by titration.

The method described is particularly useful when the substance is already dissolved, and also in the case of volatile substances. A further advantage is that, at the same time, an indication is given as to the number of methyl groups in the chain.

Since, under the conditions of the experiment, ethyl alcohol is practically quantitatively oxidised to acetic acid, the method will be particularly of value in the determination of small concentrations of alcohol, where the error on the specific gravity method is great. Moreover, alcohol could be determined in the presence of any compounds which oxidise quantitatively to carbon dioxide, such as sugars and polyhydric alcohols, without the necessity of separation by distillation. In a concentration of 0.5 per cent., and

using only 4 c.c. of the fluid, a determination of alcohol may be made by this method with an error of less than 1 per cent.

The discussion of the applications of this method to the analysis of mixtures of two fatty acids or alcohols, as well as to the determination of formates, will be reserved for a subsequent communication.

In conclusion, I would express my thanks to Professor Arthur Harden, F.R.S., for help and criticism.

THE LISTER INSTITUTE,
LONDON.

CCVII.—*Organo-derivatives of Bismuth. Part I. The Preparation and Properties of some Tertiary Aromatic Bismuthines and their Halogen Derivatives.*

By FREDERICK CHALLENGER.

THE object with which the present research was commenced was primarily the synthesis of an asymmetric organo-bismuth compound, which could be resolved into optically active components (P., 1913, 29, 76).

Such a result, however, could hardly be expected until a considerable amount of further information had been obtained regarding the properties of organo-bismuth compounds. The comparatively large number of publications dealing with this subject* have confined themselves to a very superficial examination of the compounds described, their reactions having been very little investigated. Experiments were therefore made with the object of discovering (1) the extent to which the Grignard reagent could be used in the synthesis of bismuthines, and (2) the nature of its reaction with various types of halogen bismuthines, for example, $\text{BiR}_2\text{R}_3\text{X}$, and bismuthine dihaloids of the type $\text{BiR}_2\text{R}_3\text{X}_2$. It was then found that the properties of these halogen compounds were extremely interesting, and worthy of a closer investigation.

Especially interesting and important from a theoretical point of view is the question of the stability of compounds of the type

* Löwig, *Annalen*, 1850, 75, 355; Breed, *ibid.*, 1852, 82, 106; Dunhaupt, *ibid.*, 1854, 92, 371; Michaelis and Polis, *Ber.*, 1887, 20, 52, 54; Marquardt, *Ber.*, 1887, 20, 1516; 1888, 21, 2035; Michaelis and Marquardt, *Annalen*, 1889, 251, 323; Gillmeister, *Ber.*, 1897, 30, 2843; Pfeiffer and Pietsch, *ibid.*, 1904, 37, 4620; Hilpert and Grüttner, *ibid.*, 1913, 46, 1685; Hilpert and Dittmar, *ibid.*, 3741; Ehrlich and Karrer, *ibid.*, 3564.

$\text{BiR}_1\text{R}_2\text{R}_3\text{R}_4\text{X}$ and $\text{BiR}_1\text{R}_2\text{R}_3\text{XY}$, where X and Y are similar or dissimilar halogen atoms.*

From the work of Pope and Peachey (T., 1899, 75, 1127) and Leisenheimer (Ber., 1908, 41, 3966; 1911, 44, 356), it might be expected that compounds of the types (1) $\text{BiR}_1\text{R}_2\text{R}_3\text{R}_4\text{X}$ or (2) $\text{O:BiR}_1\text{R}_2\text{R}_3$ would be capable of resolution into enantiomorphously related optically active forms.

A compound of the type (1) might conceivably be synthesised in at least two ways, namely, (a) by the addition of an alkyl or aryl haloid to an unsymmetrical bismuthine, and (b) by the action of the Grignard reagent on the dihalogen additive products of an unsymmetrical bismuthine.

As regards substances of the bismuthine oxide type, certain methods of preparation will immediately suggest themselves. Investigations in these directions are in progress.

The author has found that when triphenylbismuthine is warmed for a short time with isobutyl bromide, small quantities of diphenylbromobismuthine, BiPh_2Br , are obtained. It is just possible, although rendered still more doubtful by results now to be described, that the conditions requisite for the production in this manner of bismuthonium haloids have not yet been obtained. Further experiments in this direction are in progress.

In order to gain some idea as to the course which the reaction between an unsymmetrical compound of the type $\text{BiR}_1\text{R}_2\text{R}_3\text{Br}_2$ and the Grignard reagent might be expected to take, the behaviour of triphenylbismuthine dibromide, BiPh_3Br_2 , with magnesium ethyl bromide and magnesium phenyl bromide has been investigated.

Neither of these reactions appears to take a normal course. With magnesium phenyl bromide the products obtained consisted of triphenylbismuthine, diphenylbromobismuthine (Michaelis and Marquardt, *Annalen*, 1889, 251, 328), and phenyldibromobismuthine, BiPh_2Br_2 (see p. 2215). It is very probable that tetraphenylbismuthonium bromide is first formed, but undergoes decomposition into triphenylbismuthine and bromobenzene.

The formation of diphenylbromobismuthine is possibly due to the decomposition of the triphenylbismuthine dibromide, since the pure compound is by no means stable, and when boiled with dry benzene gives a good yield of diphenylbromobismuthine. Moreover, if pure, colourless triphenylbismuthine dibromide is heated for a few minutes at 100° , it decomposes, forming a yellow, viscid mass, which has a powerful odour of bromobenzene.

The interaction of magnesium ethyl bromide and triphenyl-

* An account of experiments with compounds of the latter type will shortly be communicated to the Society in conjunction with Mr. C. F. Allpress.

bismuthine dibromide led to results which were very similar to those just described. Triphenylbismuthine and diphenylbromobismuthine were obtained, whilst the reaction mixture had a strong odour of bromobenzene.

The formation of the first-named substance may be due to the decomposition of the unstable triphenylethylbismuthonium bromide, BiPh_3EtBr , which may first be formed, ethyl bromide being eliminated. The decomposition of phenyltrimethylarsonium iodide, which, on being heated, gives rise to methyl iodide and phenyldimethylarsine, is a somewhat similar reaction (Winmill, T., 1912, 101, 719): $\text{AsPhMe}_3\text{I} = \text{AsPhMe}_2 + \text{MeI}$.

Owing to the undoubted formation of bromobenzene, it is possible that the diphenylbromobismuthine resulted from the decomposition of the triphenylbismuthine dibromide under the influence of the Grignard reagent.

An attempt was then made to remove one of the phenyl groups in diphenylbromobismuthine by means of bromine in chloroform solution, in the hope that the resulting compound might be of use in the synthesis of the so-called mixed or unsymmetrical tertiary bismuthines. *Phenyldibromobismuthine*, crystallising in golden-yellow needles, melting at $205-206^\circ$, was thus obtained. The chloroform solution was found to contain bromobenzene (which was identified by its conversion into *p*-bromonitrobenzene) and a certain amount of bismuth bromide. The formation of phenyldibromobismuthine in the above reaction is not analogous to the behaviour of the corresponding diphenylchlorostibine, SbPh_2Cl , which was found by Morgan and Micklethwait to yield Ph_2SbCl_3 on treatment with chlorine (T., 1911, 99, 2295).

In consequence of the instability of the derivatives of quinquivalent bismuth, to which reference has already been made, and of numerous other compounds of the type R_3BiCl and R_3BiBr , which are being investigated in conjunction with Mr. C. F. Allpress, the formation of a stable compound, BiPh_2Br , was hardly to be expected.

The action of magnesium ethyl bromide on diphenylbromobismuthine was next investigated in the hope that diphenylethylbismuthine, BiPh_2Et , would be produced. The reaction, however, took a somewhat unexpected course, the only product which could be isolated being triphenylbismuthine.

Triethylbismuthine was also formed (see p. 2216), but was not isolated. The course of the reaction is possibly represented by the equation $3\text{BiPh}_2\text{Br} + 3\text{MgEtBr} = 2\text{BiPh}_3 + \text{BiEt}_3 + 3\text{MgBr}_2$.

By the action of magnesium α -naphthyl bromide on diphenylbromobismuthine, better results were obtained, *diphenyl- α -naphthyl-*

bismuthine, $\text{BiPh}_2\cdot\text{C}_{10}\text{H}_7$ (m. p. 118—119°), being readily isolated from the reaction mixture. This seems to be the first compound of the type $\text{BiR}_2\text{R}'$ to be described. With bromine it gives rise to diphenyl- α -naphthylbismuthine dibromide, $\text{BiPh}_2\cdot\text{C}_{10}\text{H}_7\cdot\text{Br}_2$ (m. p. 140°). This decomposes when heated for a short time at 100°.

Tri- α -naphthylbismuthine (m. p. 234—235°) is readily obtained by the interaction of bismuth bromide and magnesium α -naphthyl bromide. It forms a yellow, crystalline dibromide (m. p. 122°), which decomposes when kept for a short time at 100°. An account of the properties of the dibromide of this and the preceding tertiary bismuthine, and of the decompositions they may be made to undergo, will shortly be communicated to the Society.

EXPERIMENTAL.

Stability of Triphenylbismuthine Dibromide.

This substance was prepared by Michaelis and Marquardt (*loc. cit.*), who state that it melts at 122°.

Triphenylbismuthine dibromide, when twice recrystallised from cold benzene and light petroleum, separates in needles, which melt at 118° when placed in a sulphuric-acid bath (previously warmed to 80°) and heated at the usual rate. If, however, the initial temperature of the bath was 80°, and the subsequent heating carried out much more quickly, the specimen melted at 123—124°, and on another occasion at 121°.

The melting point was also found to depend to a certain extent on the size of the crystals used in the determination. This was verified several times, the powdered crystals melting from three to five degrees lower than those which had not been powdered. The melting points were determined simultaneously.

Some of the recrystallised substance (m. p. 118° on fairly slow heating) was heated with dry benzene under a reflux condenser for two hours, every trace of moisture being carefully excluded. On cooling, crystals of diphenylbromobismuthine were deposited; these melted at 152°, and after one recrystallisation at 154—156°.

On heating a specimen of the dibromide in a small sealed tube at 100° for about twenty minutes, it was found to have become yellow and pasty, and a strong odour of bromobenzene was observed.

On attempting to concentrate the mother liquor obtained in the recrystallisation of triphenylbismuthine dibromide, a deposit of diphenylbromobismuthine was obtained.

Action of Magnesium Phenyl Bromide on Triphenylbismuthine Dibromide.

Nine grams of the pure dibromide were covered with dry ether and gradually treated with a solution of magnesium phenyl bromide (1 mol.) prepared from 0.5 gram of magnesium and 2.8 grams of bromobenzene in ether. After each addition of the Grignard reagent a transient but intense purple coloration was produced, and the ether boiled. Most of the dibromide dissolved, and its place was taken by an oily solid. After about forty hours the ether was decanted from the now almost solid, insoluble residue, which was then well washed with dry ether.

(1) *Ethereal Extract and Washings.*—On evaporation, a yellow oil was left, which had an odour of bromobenzene, and partly solidified on cooling. By extraction with a mixture of ether and light petroleum, 3 grams of triphenylbismuthine were removed from this residue.

(2) *Original Residue Insoluble in Ether.*—A small portion was shaken with cold benzene, the solution filtered, and treated with light petroleum. Fine yellow crystals of diphenylbromobismuthine (m. p. 155–156°) were deposited.

The bulk of the residue was heated for about five minutes with benzene, and filtered. Yellow crystals were deposited, which sintered at 143–150°, and melted to an opaque fluid; their whole behaviour indicated that the substance was a mixture. A further deposit was obtained on addition of light petroleum; this contained some magnesium compounds.

The yellow deposits were united, and twice extracted with boiling chloroform, which removed diphenylbromobismuthine. The residue was treated with boiling benzene. The filtered extract deposited yellow needles (m. p. 206°), which did not depress the melting point of a specimen of phenyldibromobismuthine (see p. 2215).

Exactly similar results were obtained when triphenylbismuthine dibromide was heated with the Grignard reagent.

Action of Magnesium Ethyl Bromide on Triphenylbismuthine Dibromide.

Eight grams of the pure dibromide were suspended in dry ether, and a solution of magnesium ethyl bromide, prepared from 0.45 gram of magnesium and 1.9 grams of ethyl bromide, was added. The reaction became vigorous, most of the insoluble dibromide disappeared, and an oily deposit was produced. The mixture was not heated, but was kept for some days, moisture being excluded.

Similar results were, however, obtained when the reaction mixture was heated on the water-bath.

The ethereal liquid (*A*) was finally poured off from the now crystalline deposit (*B*), which was washed with ether. On evaporation of the ether from *A*, an oil was left which had a strong odour of bromobenzene, and quickly solidified. From this, 2.5 grams of pure triphenylbismuthine were extracted by means of light petroleum. The small amount of insoluble matter which remained contained compounds of magnesium and bismuth, and was not further examined.

The residue *B*, after washing with cold chloroform, weighed 2 grams. On treatment with water, about 1.5 grams remained undissolved. This was quickly separated and dried. By recrystallisation from chloroform and light petroleum, yellow crystals were deposited, which melted at 156°, and did not depress the melting point of a specimen of diphenylbromobismuthine.

Action of Bromine on Diphenylbromobismuthine.

Diphenylbromobismuthine was dissolved in dry chloroform, and treated with one molecular proportion of bromine in chloroform solution. The red colour was discharged, and a yellow precipitate formed. When collected and washed with dry chloroform, this melted at about 190°, but on recrystallisation from hot benzene fine yellow needles were obtained, melting at 205–206°, and consisting of *phenyldibromobismuthine*:

0.1510 gave 0.1266 AgBr. Br = 35.68.

$C_6H_5Br_2Bi$ requires Br = 35.95 per cent.

On distilling off the chloroform from the reaction mixture, an oil remained which had a strong odour of bromobenzene, along with a certain amount of a grey, crystalline substance. The oil was removed by repeated extractions with warm light petroleum, and found to be free from bismuth. On treatment with fuming nitric acid and addition of water to the solution, a solid was precipitated, which, after recrystallisation from alcohol, melted at 125–126°. A recrystallised specimen of *p*-bromonitrobenzene melted at 26–127°, and a mixture of the two melted at the same temperature.

The grey, crystalline solid was heated with toluene, and the filtered extract deposited crystals on cooling. These were free from organic matter, melted at about 200°, and distilled on heating strongly. The action on water and its solubility in ether showed the substance to be bismuth bromide. If the addition of bromine to diphenylbromobismuthine is continued until a per-

manent red coloration is imparted to the chloroform, the precipitate contains almost no organic matter.

Attempted Preparation of Diphenylethylbismuthine.

Five grams of diphenylbromobismuthine were treated with a solution of 0.45 gram of magnesium and 1.9 grams of ethyl bromide in dry ether. A vigorous reaction took place, most of the yellow bromide disappeared, and a dark-coloured oil was precipitated. The mixture was heated on the water-bath under reflux for about an hour. After forty-eight hours the ether was distilled off, the residue treated with water, and the insoluble matter was collected and extracted three times with alcohol. The alcoholic extract deposited large quantities of triphenylbismuthine, and the mother liquors from these deposits possessed an unbearable odour, resembling that of the alkyl compounds of tin. The alcohol which was distilled from these mother liquors also possessed the same odour. This was probably due to the presence of triethylbismuthine, which is described by Breed (*loc. cit.*) as a volatile liquid which oxidises readily in air, and possesses a disgusting odour.

Diphenyl- α -naphthylbismuthine.

A solution of magnesium α -naphthyl bromide, prepared from 17 grams of α -bromonaphthalene and 2 grams of magnesium, was treated with 26.5 grams of diphenylbromobismuthine. A fairly vigorous reaction occurred, and an almost clear solution was obtained. The mixture was then heated under reflux for two and a-half hours, and allowed to remain overnight. The ether was poured off, and the white, insoluble deposit washed with ether. On removal of the solvent, an oil was left which, after treatment with water, very slowly solidified. It probably contains a certain amount of phenyldi- α -naphthylbismuthine (arising from traces of phenyldibromobismuthine in the diphenylbromobismuthine), in addition to naphthalene and diphenyl- α -naphthylbismuthine, and is being reserved for further investigation.

The crystalline deposit, which was insoluble in ether, was warmed with water to remove magnesium salts, dried, and dissolved in chloroform. The solution deposited a crystalline substance when it was diluted with alcohol. This melted at 115–117°, and, after a few recrystallisations, at 118–119°:

0.1884 gave 0.3698 CO₂ and 0.0712 H₂O. C=53.55; H=4.18.

0.2230 „ 0.4352 CO₂ „ 0.0698 H₂O. C=53.23; H=3.48.

0.4170 „ 0.1990 Bi₂O₃. Bi=42.76.

C₂₂H₁₇Bi requires C=53.97; H=3.50; Bi=42.53 per cent.

Diphenyl- α -naphthylbismuthine is readily soluble in chloroform, benzene, or toluene, but less readily so in alcohol or ether. Warm, concentrated hydrochloric acid immediately decomposes it, yielding benzene and naphthalene.

When treated in ethereal solution with one molecular proportion of bromine, likewise dissolved in ether, the solution was immediately decolorised, and a yellow, crystalline precipitate deposited. On recrystallisation from a mixture of benzene and light petroleum, this was obtained in yellow, prismatic needles, which, when pure, melted at 140° .

As in the case of other bismuthine dibromides described in this paper, the substance melts when heated for a few minutes in a sealed tube at 100° . On cooling, it remains pasty, and an odour resembling that of α -bromonaphthalene is very apparent. Towards hot concentrated hydrochloric acid the dibromide is relatively stable.

Tri- α -naphthylbismuthine.

Magnesium α -naphthyl bromide (3 mols.), prepared from 1.6 grams of magnesium and 13.7 grams of α -bromonaphthalene, was treated with 11 grams of anhydrous bismuth bromide, dissolved in the minimum quantity of dry ether. A vigorous reaction occurred, and a yellow precipitate was formed, which disappeared on shaking; simultaneously, a large quantity of solid matter was deposited. The mixture, after remaining overnight, was heated for one and a-half hours on the water-bath, after which the ether was distilled off, and the residue treated with water. The solid matter which remained was collected and dried. This product was repeatedly extracted with chloroform, the extracts united, concentrated somewhat, and treated with alcohol, when a slightly yellow, crystalline deposit was obtained. On recrystallisation from a mixture of chloroform and alcohol the substance was finally obtained in almost colourless needles, melting at 235° :

0.2152 gave 0.4803 CO_2 and 0.0728 H_2O . $\text{C}=60.87$; $\text{H}=3.76$.

0.3150 „ 0.1253 Bi_2O_3 . $\text{Bi}=35.66$.

$\text{C}_{20}\text{H}_{21}\text{Bi}$ requires $\text{C}=61.10$; $\text{H}=3.60$; $\text{Bi}=35.30$ per cent.

Tri- α -naphthylbismuthine is fairly readily soluble in chloroform, carbon tetrachloride, benzene, or toluene, sparingly so in hot alcohol, and almost insoluble in ether or light petroleum. Hot concentrated hydrochloric acid decomposes it quantitatively, bismuth chloride and naphthalene being produced.

Tri- α -naphthylbismuthine Dibromide.

1.4 Grams of tri- α -naphthylbismuthine in chloroform were slowly treated with a solution of 0.3 gram of bromine in the same solvent. Decolorisation took place immediately, and on adding light petroleum, a yellow, crystalline substance was obtained in almost theoretical yield (1.65 grams). On recrystallisation, the melting point was found to depend on the rate of heating, and was usually about 119–121°, although when very slowly heated, readings as low as 110° were obtained. The cause of this lies in the instability of the pure substance, since, when heated in a small sealed tube at 100°, decomposition set in. After ten minutes the whole was found to be pasty, and the odour of α -bromonaphthalene was very noticeable.

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CCVIII.—*The Condensation of Furan-2:5-dialdehyde
with Malonic Ester and Malonic Acid.*

By WILLIAM FRANCIS COOPER and WALTER HAROLD NUTTALL.

THE authors have for some time past (compare T., 1911, **99**, 1193; 1912, **101**, 1074) been engaged in a more or less systematic investigation of the furan group, and the present communication deals with the condensation of furan-2:5-dialdehyde with malonic ester and malonic acid. The object of such condensations was to determine whether they followed a normal course. The condensation of ω -bromomethylfurfuraldehyde with malonic ester is so obscure that, in spite of much investigation, it still remains unexplained. The condensation takes place in different ways, according as to whether hydroxyl ions are present or absent. In the absence of hydroxyl ions, a pale yellow, crystalline compound, melting at 99.5–100°, the composition of which has not yet been determined, is produced. When the condensation is carried out in the presence of hydroxyl ions, a beautiful blue, fluorescent solution is formed (Fenton, T., 1898, **73**, 554), from which, however, it has not yet been possible to isolate the fluorescent compound.

Although the condensation of furandialdehyde and malonic ester does not give fluorescent compounds, there was the possibility that the condensation might not be normal, and so might throw some light on that of the bromo-aldehyde and malonic ester.

Whilst this investigation failed in its original purpose, normal condensation products being obtained, a peculiar additive property of one of the condensation products has been observed.

Furandialdehyde condenses with two molecules of ethyl malonate, giving *ethyl furan-2:5-dimethylenemalonate* (I). This ester on hydrolysis gives the corresponding tetracarboxylic acid (II):



It is this tetracarboxylic acid that possesses the curious additive properties referred to above. When dried at 100°, or crystallised from dry ether, it is obtained in the anhydrous state, and is then canary-yellow. When crystallised from water it combines with one molecule of water, and is then reddish-orange to brown, according to the rapidity with which it separates from solution.

When the anhydrous acid is crystallised from glacial acetic acid, a compound of the two acids is produced, which is pentabasic and distinctly dark brown. This compound consists of one molecule of the tetracarboxylic acid combined with one molecule of acetic acid, but the state of combination appears to be unstable, as, on distilling an aqueous solution of the compound, acetic acid is evolved.

Another peculiar compound of the tetracarboxylic acid with acetic acid has been obtained by the condensation of furandialdehyde with malonic acid. When acetic acid is used as catalyst, a red, crystalline acid is produced. This is isomeric with the dark brown acid obtained by crystallising the anhydrous, yellow tetracarboxylic acid from glacial acetic acid. Further, this red acid is pentabasic, and also consists of one molecule of the tetrabasic acid combined with one molecule of acetic acid. In this case, also, the acetic acid is in an unstable state of combination, as acetic acid is evolved on boiling an aqueous solution of the red acid. In fact, the two acids appear to be identical in all their properties with the exception of colour of their crystals. This difference is quite distinct, and the acids retain their respective colour even on repeated crystallisation from glacial acetic acid. In solution, the difference in colour of the two acids is less marked. It is still appreciable in their acetic acid solution, but entirely disappears in their aqueous solutions, which are yellow, and quite indistinguishable from each other. This probably indicates that, in aqueous solution, both acids are dissociated into the same yellow tetracarboxylic acid and acetic acid.

Neither the brown nor the red acid melts, but on heating both

become yellowish-brown, acetic acid is evolved, and a crystalline, yellow sublimate formed.

On esterifying with alcohol and hydrogen chloride, both the red and the brown pentabasic acids, as well as the yellow tetrabasic acid, give the same tetracarboxylic ester, melting at 90–91°, which is identical with the condensation product of furandialdehyde and malonic ester.

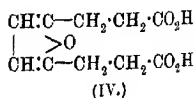
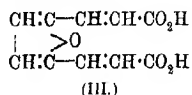
It is of interest to note that this tetracarboxylic ester may be crystallised from glacial acetic acid without change. The ability to combine with one molecule of acetic acid appears to be confined to the tetracarboxylic acid alone; it is not possessed by its ester, nor by the corresponding diacrylic acids, nor by reduction products of the latter.

No satisfactory explanation of this peculiarity or of the isomerism of the brown and red pentabasic acids can be advanced at present.

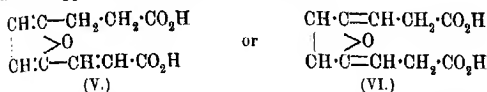
In view of the similarity in structure of furan and pyrone, the furan oxygen atom might conceivably become quadrivalent and combine with acetic acid, but this would not explain the isomeric forms or the inability of the ester and diacrylic acids, etc., to combine with acetic acid. Further, if this were the correct explanation, it would be expected that the tetracarboxylic acid would combine with other compounds, such as methyl iodide, hydroferrocyanic acid, etc., but all attempts to bring about such combinations have failed.

The condensation of furandialdehyde with malonic acid (as opposed to malonic ester) gives different products, according to the catalyst employed. With glacial acetic acid as catalyst, the pentabasic red acid, described above, is produced; with pyridine as catalyst, however, there is a loss of carbon dioxide, and a brown powder, consisting chiefly of one or more furandiacrylic acids, is obtained. Although pure *furandiacrylic acid* (III) may be easily obtained in the crystalline condition, it has been found impossible to obtain directly a crystalline diacrylic acid from the brown condensation product, which probably consists of a mixture of isomeric furandiacrylic acids, three of which are theoretically possible.

The brown condensation product on esterification gives a well-defined, crystalline ester, whilst reduction with sodium amalgam in alkaline solution gives *furandiacrylic acid* (IV), which is also crystalline.



If the reduction, however, is carried out with aluminium filings, an intermediate acid, containing two atoms of hydrogen more than the diacrylic acid, is produced, although furandipropionic acid is the final product. The constitution of this intermediate acid might be suggested by either of the formulæ:



On oxidation with concentrated nitric acid, (V) should give the well-known dehydromucic acid. The white, crystalline acid actually obtained, however, was certainly not dehydromucic acid, as it was extremely soluble in water, and did not give the very characteristic reaction with ferric chloride; further, it melted indistinctly at about 170°, and, on further heating, evolved fumes, which were extremely irritating to the throat. Hence it would appear that formula (VI) is more feasible.

An attempt to rupture the furan ring in furandipropionic acid by Marckwald's method (*Ber.*, 1887, 20, 2811; 1888, 21, 1398) and produce a derivative of *n*-decane, showed that the ring was stable under these conditions. The dipropionic acid was heated with alcoholic hydrogen chloride on a water-bath for six hours without effect. Bromine water, on the other hand, readily decomposes it, giving an acid of high melting point, containing bromine, the investigation of which is not yet complete, the reaction of furan compounds with bromine water being apparently very erratic.

EXPERIMENTAL.

Condensation of Furan-2:5-dialdehyde with Ethyl Malonate.

Ethyl Furan-2:5-dimethylenemalonate (I).

Five grams of furan-2:5-dialdehyde (1 mol.) are heated with 13 grams of ethyl malonate (2 mols.) and 13 grams of acetic anhydride (3 mols.) on a sand-bath under an air condenser for eight hours. After cooling somewhat, excess of water is added, and, after remaining overnight, the mixture is rendered slightly alkaline with sodium carbonate and extracted with ether. The ether is distilled off, and the product purified by recrystallisation from alcohol, and finally from hot light petroleum. From alcohol it crystallises in pale yellow, transparent, highly refractive octahedra, which melt at 90–91°:

0.2002 gave 0.4338 CO₂ and 0.1049 H₂O. C=59.09; H=5.82.

C₂₀H₂₄O₈ requires C=58.82; H=5.88 per cent.

It is readily soluble in the usual organic solvents, with the exception of cold petroleum, and is insoluble in water, but dissolves in concentrated sulphuric acid with a yellow colour. It can be crystallised from glacial acetic acid without change. It does not combine with acetic anhydride in the presence of ferric chloride.

The acid can be boiled with concentrated hydrochloric acid without change, but is readily hydrolysed by hot alkali hydroxides.

Treatment with excess of bromine in carbon tetrachloride gives a crystalline bromo-derivative, melting at 87.5° , but the exact conditions for obtaining this have not been determined.

Furan-2: 5-dimethylenemalonic Acid (II).—The ethyl ester (I) is boiled with excess of sodium hydroxide solution (D 1.3). The crystals at first melt, and then dissolve, with considerable evolution of heat. The dark, reddish solution is cooled, acidified, and completely extracted with ether or ethyl acetate. The yellow, ethereal extract cannot be dried, owing to the readiness with which the acid is adsorbed, especially by sodium sulphate. After distilling off the solvent, the residue is dissolved in a little warm water, filtered, and the filtrate allowed to evaporate in a vacuum desiccator. The tetracarboxylic acid crystallises from water with approximately 1 molecule of water of crystallisation, which, however, is slowly given up at the ordinary temperature, especially in a vacuum desiccator. When the hydrated acid is dried at 100° , the change in colour from a reddish-orange to a canary-yellow is most marked. For analysis the anhydrous acid, dried at 100° , was used:

0.3370 gave 0.6026 CO_2 and 0.0860 H_2O . $\text{C} = 48.76$; $\text{H} = 2.83$.

$\text{C}_{12}\text{H}_8\text{O}_8$ requires $\text{C} = 48.65$; $\text{H} = 2.70$ per cent.

0.2055 Gram required 27.4 c.c. of $N/10$ -sodium hydroxide for complete neutralisation, whilst the theoretical amount for a tetrabasic acid of this formula is 27.8 c.c. The acid readily loses carbon dioxide, which probably explains the somewhat low figure obtained on titrating.

The acid is readily soluble in water, giving a yellow solution, which becomes dark reddish-brown on the addition of ferric chloride solution. On boiling, a reddish, flocculent precipitate is produced. With an aqueous solution of the ammonium salt of the acid, silver nitrate gives an amorphous, canary-yellow precipitate; calcium chloride, a yellowish-brown precipitate on boiling; copper sulphate, a brown, gelatinous precipitate, especially on boiling; normal lead acetate, a pale yellow precipitate in the cold.

Additive Compound of Furan-2:5-dimethylenemalononic Acid with Acetic Acid. ("Brown Acid.")

When crystallised from glacial acetic acid, the tetracarboxylic acid is converted into a brown, crystalline acid, which is quite distinct in appearance from the original yellow acid, a distinction which is not affected by repeated recrystallisation from acetic acid. Both the combustion and titration with *N*/10-alkali indicate that these brown crystals consist of one molecule of the tetracarboxylic acid and one molecule of acetic acid:

0.2000 gave 0.3447 CO_2 and 0.0624 H_2O . $\text{C}=47.01$; $\text{H}=3.47$.

$\text{C}_{12}\text{H}_8\text{O}_{10}, \text{C}_2\text{H}_4\text{O}_2$ requires $\text{C}=47.19$; $\text{H}=3.37$ per cent.

0.1524 Gram required 21.4 c.c. *N*/10-alkali, which is the amount required by a pentabasic acid of this formula.

The brown acid is not sufficiently soluble in glacial acetic acid for its molecular weight to be determined in that solvent by the freezing-point method. It dissociates in water, as, on distilling an aqueous solution, acetic acid passes over. It is insoluble in benzene or ethylene dibromide, so that these cannot be used for molecular-weight determinations.

The acid is soluble in water to a yellow solution, which is changed to a dark reddish-brown on the addition of ferric chloride solution. On heating the mixture, a copious, amorphous precipitate is produced, which is distinctly browner than the corresponding precipitate with the yellow acid. An aqueous solution of the ammonium salt gives an amorphous, canary-yellow precipitate with old silver nitrate, and a yellow precipitate with calcium chloride on boiling. These precipitates are practically indistinguishable from those given by the ammonium salt of the yellow acid.

Condensation of Furandialdehyde with Malonic Acid.

(a) With Glacial Acetic Acid.

Additive Compound of Furan-2:5-dimethylenemalononic Acid with Acetic Acid. ("Red Acid.")

Five grams of furandialdehyde (1 mol.) and 8.4 grams of malonic acid (3 mols.) are dissolved in 20 c.c. of glacial acetic acid, and the solution is heated on a water-bath under reflux for six to seven hours. The acetic acid is then distilled off under diminished pressure, and the dark residue extracted with ether. After drying the extract, the ether is distilled off, and a red, crystalline acid is obtained. This is conveniently purified by twice recrystallising from glacial acetic acid:

0.2009 gave 0.3473 CO_2 and 0.0653 H_2O . $\text{C}=47.15$; $\text{H}=3.61$.

$\text{C}_{12}\text{H}_8\text{O}_9, \text{C}_2\text{H}_4\text{O}_2$ requires $\text{C}=47.19$; $\text{H}=3.37$ per cent.

This red acid is therefore isomeric with the brown acid obtained by recrystallising the yellow tetracarboxylic acid from glacial acetic acid. The red acid is also pentabasic.

0.2053 Gram required 29.1 c.c. $N/10$ -sodium hydroxide, whilst a pentabasic acid of this formula requires 28.8 c.c.

(b) With Pyridine. *Furan-2:5-diacrylic Acid.*

Five grams of furan-2:5-dialdehyde (1 mol.) are dissolved in a little alcohol, 8.4 grams of malonic acid (2 mols.) dissolved in the solution, and 8.4 grams of pyridine (2.6 mols.) added. The mixture is heated on a water-bath under reflux for six to seven hours, cooled, and poured into cold 10 per cent. sulphuric acid, when a pale brown, amorphous precipitate is formed, consisting of crude furandiacrylic acid. No direct method of purifying it has been found. It is probably a mixture of stereoisomerides. Up to the present, a pure acid has only been obtained by esterification of the acid, and subsequent hydrolysis of the purified ester with sodium ethoxide. A pale yellow, amorphous powder is thus obtained, which crystallises from acetic acid in colourless crystals, free from acetic acid:

0.2054 gave 0.4343 CO_2 and 0.0725 H_2O . $\text{C}=57.67$; $\text{H}=3.92$.

$\text{C}_{20}\text{H}_8\text{O}_6$ requires $\text{C}=57.69$; $\text{H}=3.84$ per cent.

Furan-2:5-diacrylic acid does not melt. It is soluble in hot water, but insoluble in cold. It is insoluble in all the usual organic solvents except acetone and acetic acid. It readily combines with bromine.

Ethyl Furan-2:5-diacrylate.—The acid may be esterified by dissolving in absolute alcohol and saturating with hydrogen chloride, but the yield is very erratic, and much tarry matter is frequently produced. It is best prepared from the acid chloride, a yellow, crystalline solid, readily obtained by the action of thionyl chloride on the crude, brown, amorphous acid. The acid chloride is treated with excess of absolute alcohol in the cold, and crystals of the required ester separate from the product on keeping. It is purified by recrystallisation from carbon tetrachloride or light petroleum, from which it separates in flat, shiny, transparent, colourless plates, melting at 110 – 111° , and soon becoming white and opaque:

0.1985 gave 0.4625 CO_2 and 0.1061 H_2O . $\text{C}=63.55$; $\text{H}=5.94$.

$\text{C}_{14}\text{H}_{16}\text{O}_6$ requires $\text{C}=63.63$; $\text{H}=6.06$ per cent.

Methyl Furan-2:5-diacrylate.—This was prepared by esterifying the crude acid with methyl alcohol and hydrogen chloride. It

crystallises from carbon tetrachloride or light petroleum in white, shiny flakes, melting at 152—153°.

Reduction of the Brown, Amorphous Furandiacrylic Acid.

(a) *With Sodium Amalgam. Furan-2:5-dipropionic Acid.*

The crude diacrylic acid is dissolved in 10 per cent. sodium hydroxide solution, and sodium amalgam added from time to time, the reduction being continued until a test portion gives no further precipitate on acidifying. This is usually the case in five to six hours. After acidifying, the reduced acid is extracted with ether. The acid is purified by recrystallisation from water, and is obtained in glistening lamellæ, melting at 151—152°. The acid distils without decomposition:

0.1991 gave 0.4135 CO_2 and 0.1039 H_2O . $\text{C}=56.64$; $\text{H}=5.80$.

$\text{C}_{10}\text{H}_{12}\text{O}_5$ requires $\text{C}=56.60$; $\text{H}=5.66$ per cent.

0.4051 Gram required 38.2 c.c. *N*/10-sodium hydroxide for neutralisation. If the acid is dibasic, its molecular weight is 212.1. $\text{C}_{10}\text{H}_{12}\text{O}_5$ requires M.W.=212.

The acid is soluble in water, alcohol, ether, ethyl acetate, benzene, or chloroform, but insoluble in light petroleum. It does not give a jelly on boiling with ferric chloride solution (difference from lehydromucic acid).

It is stable to boiling alcoholic hydrogen chloride, but its aqueous solution is readily attacked by bromine water. It can be recrystallised from glacial acetic acid without change.

(b) *With Aluminium Powder. Furan-2-propionic-5-acrylic Acid (?)*.

The crude furandiacrylic acid is dissolved in 10 per cent. sodium hydroxide solution, and aluminium powder added to the slightly warm solution. The reduction is allowed to continue overnight. As reduction proceeds, the colour of the solution becomes somewhat paler. The aluminium and precipitated alumina are filtered off, and sufficient acid is added to the filtrate to dissolve the alumina at first precipitated. On extracting with ether, a mixture of the two reduction acids is obtained, furandiacrylic acid largely preponderating. The two acids are readily separated by recrystallisation from hot water, in which furan-2-propionic-5-acrylic acid is only sparingly soluble. After one or two recrystallisations from water, with the use of animal charcoal, it is obtained in white, shining plates, melting at 183—184°:

0.2010 gave 0.4228 CO_2 and 0.0894 H_2O . $\text{C}=57.37$; $\text{H}=4.93$.

$\text{C}_{10}\text{H}_{10}\text{O}_5$ requires $\text{C}=57.14$; $\text{H}=4.76$ per cent.

It is soluble in alcohol, acetone, or ethyl acetate, almost insoluble in light petroleum or benzene, sparingly soluble in chloroform, soluble in hot water, but almost insoluble in cold. It can be recrystallised unchanged from glacial acetic acid.

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CCIX.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part VII. Some Esters of the Carbinols of the Formula $C_2H_5 \cdot CH(OH) \cdot R$.*

By JOSEPH KENYON.

ONE of the most interesting suggestions that has been put forward with the object of bringing a little order and system into the large field of optically active substances, particularly when several such substances constitute a homologous series, is that of Frankland (T., 1899, 75, 368). It is concisely expressed by its author thus: "According to the commonly accepted views of stereochemistry, a continuous chain of five carbon atoms will all but return on itself, and, beyond this, further additions to the chain will lead to such interference as must necessitate a readjustment of the exact positions occupied by the carbon atoms in a shorter chain. It is surely highly probable that this stereochemical change should be betrayed by some irregularity in the rotatory manifestations, for example, by the exhibition of a maximum rotation in those series in which the ascent of the series leads to an increase in the rotatory power."

In Part IV. of this series of investigations (T., 1913, 103, 1923) a series of alcohols of the general formula $C_2H_5 \cdot CH(OH) \cdot R$ was described which exhibited well-defined maxima on the curve connecting the molecular rotatory powers and molecular weight, when the number of carbon atoms in the growing chain R was 5 and 6 or 10 and 11. This afforded very definite evidence of the correctness of Frankland's view, and with the object of seeking further confirmation of this view the *acetates* and the *n-heptoates* of this series of alcohols have been prepared and carefully investigated.

Moreover, in Part V. of this series (this vol., p. 830) a large number of esters of the carbinols of the formula $CH_3 \cdot CH(OH) \cdot R$ were described; in the various homologous series of these esters, ranging in each case from the acetate to the stearate, it was found

generally that the specific rotatory powers of the different members any one series rose to a maximum for the *n*-valerate, and after it fell steadily for the succeeding members of the series.

It will be noticed that this second case is quite different from the first one in that the growing chain ($\text{CO}\cdot\text{R}$, the acyl group) is *not directly* attached to the asymmetric carbon atom, but only by means of the intervening oxygen atom, whereas in the case of the "ethyl" series of carbinols the growing chain $\cdot\text{R}$ is *directly* attached to the asymmetric carbon atom.

In order to see if any additional evidence could be obtained as to the applicability of Frankland's suggestion to a homologous series of esters derived from one and the same alcohol, there has now been prepared a number of esters of *d*- γ -nonanol ranging from the acetate to the stearate.

It is remarkable that, with the exception of the derivatives of ethylethylcarbinol and ethylpropylcarbinol, all the esters described in this paper have in the homogeneous state rotatory powers of opposite sign to those of the parent alcohols, and do not exhibit under any of the experimental conditions tried anomalous dispersion, whilst in no instance is there any apparent reason to suppose that esterification has been accompanied by a change in the configuration of the molecule.

These compounds afford a very good example to show that a very small change in chemical constitution may bring about a large alteration in optical rotatory power. The seventy-three esters prepared from the carbinols of the formula $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{R}$ (see Part V.) had in the homogeneous state at the ordinary temperature rotatory powers of the same sign as that of the parent alcohols, whereas in the esters now described the replacement of the methyl group by the ethyl group causes a change of sign from that of the rotatory powers of the parent alcohols.

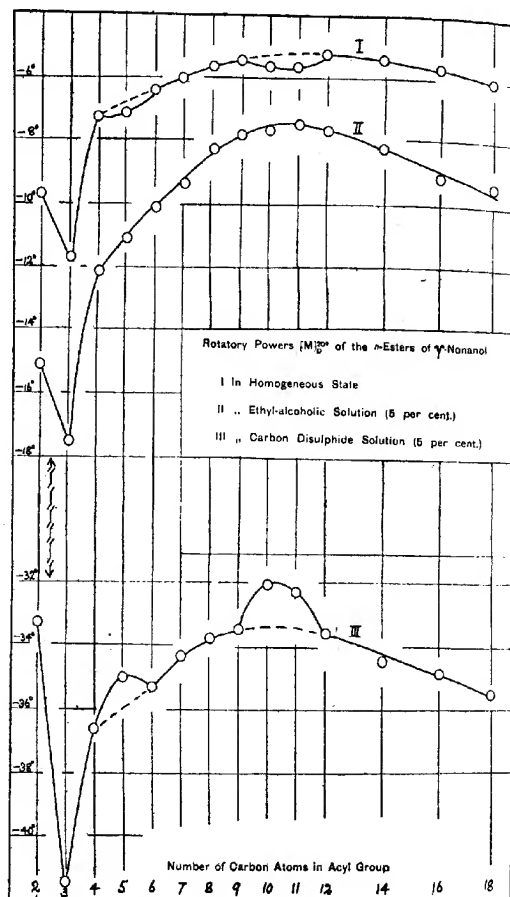
On referring to the first curve in Fig. 1, it will be noticed that the molecular rotatory powers, $[\text{M}]_D^{20}$, of the normal esters of *l*- γ -nonanol,* when measured in the homogeneous state, lie on a curve which exhibits deviations from regularity at the positions for the *n*-valerate, and also for the *n*-decoate and *n*-undecoate.

It will be seen from the second curve in the same diagram that the molecular rotatory powers of the esters, $[\text{M}]_D^{20}$, determined in approximately 5 per cent. ethyl-alcoholic solution, lie on a curve which is somewhat similar in character to the curve representing

* Throughout this paper the letters *d*- and *l*- prefixed to the name of a substance are intended to indicate merely the *sign* of the rotation of the substance, and not any views as to the relative configurations of the carbinols and their respective esters.

the molecular rotatory powers of the esters in the homogeneous state, but differs from it in not showing any deviations from strict

FIG. 1.



regularity at the positions for the valerate or the decaate and undecoate.

The third curve in the diagram was obtained by plotting the

molecular rotatory powers, $[M]_D^{20}$, of the esters determined in approximately 5 per cent. carbon disulphide solution. This curve exhibits well-defined deviations from regularity at the positions for the valerate and for the decoate and undecoate, but whilst the general character of the curve is similar to that of the two others, it will be noticed that the deviations from regularity are in an opposite sense to those exhibited by the first curve.

Regarding these deviations as mere changes in the more or less regular variation of the magnitude of the molecular rotatory power, these results may be tabulated thus:

- (1) In the homogeneous state, a special exaltation.
- (2) In ethyl-alcoholic solution, no irregularity.
- (3) In carbon disulphide solution, a special depression is shown at the positions in the series where the member (or members) contains a growing chain with five and ten (or eleven) carbon atoms respectively.

In the homogeneous state, similar curves showing exaltations at the valerate and at the decoate and the undecoate were obtained when the molecular rotatory powers were determined for the green light and for the violet light of the mercury vapour lamp.

Curves of a similar character and showing similar exaltations were also obtained when the determinations were carried out on the substances in the homogeneous state at a temperature of 100° with each of the three lights mentioned. It is thus seen that the exaltation is independent (at any rate between the limits determined) of the wave-length of the light employed, and also of the temperature at which the substances are examined.

In the ethyl-alcoholic solutions, the determinations of the molecular rotatory power of the esters for the green light of the mercury vapour lamp when plotted were all found to lie on a quite regular curve similar to that for the sodium-light determinations, but in the determinations with violet light the curve was found to exhibit well-defined depressions at the values for the hexoate and also for the decoate and undecoate.

The solutions of the esters in carbon disulphide when examined with green light were found to give a curve for their molecular rotatory powers which exhibited a well-defined exaltation at the position for the valerate, and also a well-defined depression at the positions for the decoate and the undecoate. On the other hand, when these same solutions were examined with violet light the curve for the molecular rotatory powers showed exaltations at the positions for both the valerate and the undecoate.

Although this evidence is somewhat scanty, it would thus appear that, under certain conditions, some members of a homologous

series, owing to their special stereochemical configuration, exhibit deviations, not only from what may be called the normal molecular rotatory power, but also irregular variations in the dispersive power, which is, as a rule, constant throughout a series.

In an attempt to find a relation between temperature and rotation (T., 1913, 103, 156), Patterson suggests that the values of the rotations of a number of substances of closely related constitution will all be found to lie on a series of sine curves of the form $\alpha = e^{-at} \sin(bt + c)$.

From the data given in the experimental part of this paper, it will be found that the rotations for light of three different wavelengths of practically all of the esters described in this communication—which have been determined over a range of nearly 200°—lie on curves which, within the limits of experimental error, are straight lines. It would thus appear that the curves of which these straight (or very nearly straight) lines are postulated by Patterson to form a part must be of very great amplitude indeed.*

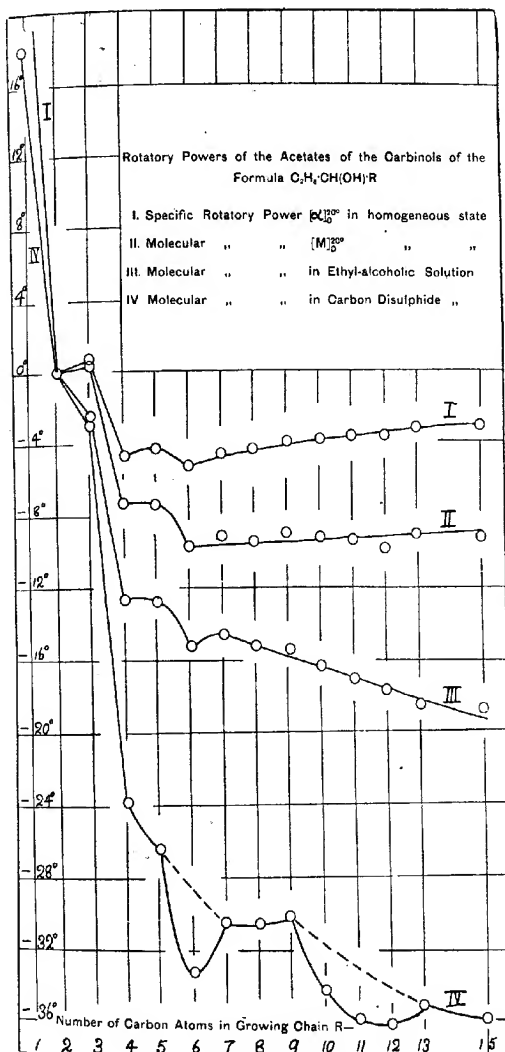
Dealing now with the acetates of the carbinols of the series $C_2H_5 \cdot CH(OH) \cdot R$, it will be seen from Fig. 2 that the curves for values for both the specific and the molecular rotatory powers, determined in the homogeneous state at 20°, are altogether different from those for the specific and molecular rotatory powers of the carbinols from which the acetates are derived (see Part IV, pp. 1924, 1926). Whereas the curves for the molecular rotatory powers of the carbinols, both in the homogeneous state and in solution, exhibit well-defined exaltations at the positions where the growing chain R contains 5 or 6 and 10 or 11 carbons, it will be seen that in the curves for the molecular rotatory powers of the acetates, measured both in the homogeneous state at 20° and in ethyl-alcoholic solution, there are no such well-defined exaltations. After the somewhat erratic values for the first few members of the series, there is a slight exaltation at the position for the acetate of ethylamylcarbinol (that is, where R contains 5 carbon atoms), but after that the values for the remaining members of the series all lie on a curve which is very nearly a straight line.

When the molecular rotatory powers of the acetates are determined in carbon disulphide solution they are found to give a

* The temperature-rotation curves for these esters, being straight lines, can be thrown into the form of the equation: $y = mx + c$.

It is then found that when the values for c are plotted against molecular weight a perfectly regular curve is obtained. If, however, the values for m are plotted in the same way, the regularity of the slope of the curve is markedly interrupted at the values for the valerate and hexoate and again at those for the decanoate and undecanoate.

FIG. 2.



curve which does to some extent resemble the curve for the molecular rotatory powers of the parent carbinols in that it does exhibit small depressions at the positions where the growing chain (R) contains 6 and 10, 11 and 12 carbon atoms respectively.

For purposes of comparison, the *n*-heptoates of a number of the carbinols of the series $C_2H_5 \cdot CH(OH) \cdot R$ were also prepared, and their molecular rotatory powers determined in ethyl-alcoholic and carbon disulphide solution. The curves which they give on plotting are similar in character to those given by the molecular rotation values of the acetates of the same series of carbinols, but show some indications of a depression (in magnitude) occurring at the positions where the growing chain (R) contains 5 and 11 carbon atoms respectively.

It thus appears that one of the effects of introducing an acyl group into the members of a homologous series of optically active alcohols of simple constitution is to produce a homologous series of esters in which the specific action of the growing chain on the molecular rotatory powers of the compounds is to a great extent nullified—possibly owing to a readjustment of the relative positions of the four atoms or groups of atoms attached to the asymmetric carbon atom in each case.

It is perhaps of interest to note in this connexion that the difference between the magnitudes of the molecular rotatory powers, $[M]_D^{20}$, in the homogeneous state of the parent alcohols and of the corresponding acetates varied from -19° (approximately) in the case of *d*-β-butanol through zero for diethylcarbinol to $+4^\circ$ for *d*-γ-hexanol, and then, increasing rapidly, gives values which vary between $+16.8^\circ$ and $+22.6^\circ$. When these values are plotted, the curve is found to exhibit distinct exaltations at the positions where the growing chain R contains 6 and 10, 11 and 12 carbon atoms respectively.

This, of course, follows from the relations described in Part IV. between the magnitudes of the molecular rotatory powers, $[M]_D^{20}$, of the carbinols in the homogeneous state and what has been stated above for those of their acetates.

In a very interesting note (P., 1913, **29**, 357), Clough* deals

* Clough states that "the dextrorotatory carbinols of the two series may be configuratively represented by the formulæ



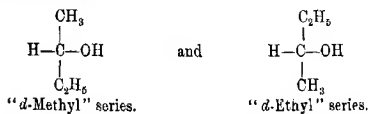
with the configuration of the optically active normal secondary alcohols described in Parts I. and IV. of this series of investigations; these two series of carbinols have, respectively, the general formulæ $\text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \text{R}$ and $\text{C}_2\text{H}_5 \cdot \text{CH}(\text{OH}) \cdot \text{R}$, and Clough suggests that dextrorotatory methylethylcarbinol is the first member of the "*d*-methyl" series, and that levorotatory methylethylcarbinol is the first member of the "*d*-ethyl" series, the symbol "*d*" being here used to denote the configuration.

It was thought that the investigation of the series of acetates described in this present paper would have furnished some definite evidence as to the correctness or otherwise of the view put forward by Clough. As a matter of fact, so far as the rotations of the homologous series of acetates are concerned, the evidence is not very conclusive, as the following considerations show.

In the homogeneous state, the acetate of dextrorotatory methylethylcarbinol ("*γ*," otherwise *β*-butanol) is of positive rotation, and the acetate of diethylcarbinol is, of course, inactive, whilst the acetates of the dextrorotatory carbinols from ethylbutylcarbinol (*γ*-heptanol) on to ethylpentadecylcarbinol (*γ*-octadecanol) are all of negative rotation. The values for the rotatory powers of these esters all lie on a continuous curve which passes through a zero value at the acetate of diethylcarbinol; but the acetate of dextrorotatory ethylpropylcarbinol (*γ*-hexanol) is positive in rotation,* and hence, in order to fit this point on the curve, it is necessary for the curve to have a second zero value lying somewhere between the positions for the acetates of *γ*-hexanol and *γ*-heptanol, and for this there is apparently no theoretical justification.

When, however, the acetates of the above series have their

and that the simplest optically active members of the two series may therefore be represented by the formulæ



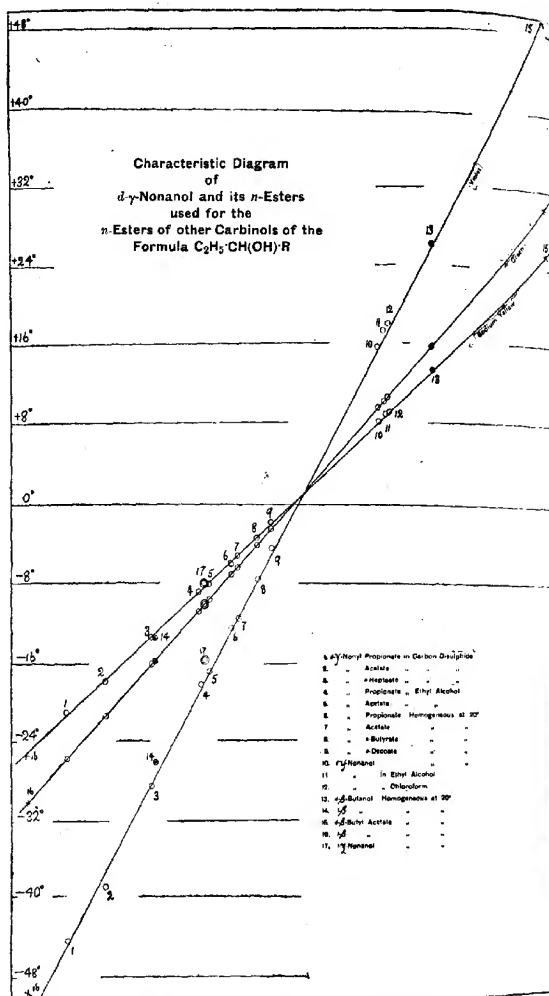
It seems to the present author, however, that there is no reason why, if the formula for the "*d*-Methyl" series is taken as given above, the formula for the

"*d*-Ethyl" series should not be $\text{HO}-\overset{\text{C}_2\text{H}_5}{\underset{\text{R}}{\text{C}}}-\text{H}$ instead of the one given by Clough,

in which case dextrorotatory methylethylcarbinol would be the first optically active member of both of the "*d*"-series of carbinols.

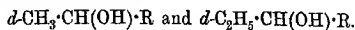
* See section in the experimental part on the resolution of ethylpropylcarbinol.

FIG. 3 *



* This characteristic diagram, which was constructed from the specific rotation data of *d*- γ -nonanol and its esters and also of the other esters described in this paper, is here used in order to show that it is highly probable that dextro-

molecular rotatory powers determined in solution (ethyl alcohol or carbon disulphide), it is found that the rotation of the acetate of dextrorotatory ethylpropylcarbinol (γ -hexanol) is of opposite sign to that of the parent carbinol, and thus makes the curve for the rotation values of the acetates quite continuous and regular. Thus it would seem that, for rotatory powers determined in solution at any rate, dextrorotatory β -butanol is the first member of each of the series of carbinols



In Parts V. and VI. of this series it was shown that the specific rotatory values of whole series of derivatives of some one parent (or series of parent) optically active alcohol—as well as the specific rotatory values of the parent alcohol itself—could be made to fit on a “characteristic diagram,” a device due to Armstrong and Walker (*Proc. Roy. Soc.*, 1913, [A], 88, 388). It was found, moreover, that rotation values of only one enantiomorphous form of an optically active compound and its derivatives would fit on one characteristic diagram; the rotation values for the other enantiomorphous form of the alcohol and its derivatives were found to fit on a second characteristic diagram which is the mirror image of the first one.

This seems to afford a rough method of finding out whether in a given group of homologous compounds all have the same configuration. To take a particular case, the characteristic diagram for the esters of dextrorotatory γ -nonanol has been constructed (Fig. 3); on this diagram there will lie the specific rotation values of dextrorotatory γ -nonanol, of its esters, and also of the acetates and heptoates described in this communication, including the acetate of dextrorotatory methylethylcarbinol and the carbinol itself, provided that all these substances have the same configuration.

If, now, the rotation values of levorotatory γ -nonanol, of levorotatory methylethylcarbinol and of its acetate are obtained (by merely arbitrarily changing the signs of the rotations of the dextrorotatory compounds), it is found that they do not fit on the

rotatory β -butanol has the same configuration as the other dextrorotatory carbinols of the ethyl series. The points 13 and 15 represent the specific rotatory values of d - β -butanol and d - β -butyl acetate respectively, and it will be seen that they lie on the diagram; on the other hand, the points 14 and 16, which represent the specific rotatory values of l - β -butanol and l - β -butyl acetate, are seen not to fit on the diagram.

The points 10 and 17 represent the specific rotatory values of d - γ -nonanol and l - γ -nonanol respectively, and of these it is seen that only the first fits on the diagram.

characteristic diagram thus drawn, but do fit on a diagram which is the mirror image of the first one.

This method of plotting gives results, then, which go to support the evidence of the molecular rotation values of the acetates observed in solution, that despite the purely theoretical speculations of Clough, dextrorotatory methylethylcarbinol is the first member, not only of the "*d*-methyl" series, $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{R}$, but also of the "*d*-ethyl" series, $\text{C}_2\text{H}_5\cdot\text{CH}(\text{OH})\cdot\text{R}$.

EXPERIMENTAL.

Resolution of Various Carbinols of the Series $\text{C}_2\text{H}_5\cdot\text{CH}(\text{OH})\cdot\text{R}$.

For the purpose of this investigation it was in many cases necessary to repeat the resolutions of the carbinols dealt with in Part IV. of this series of investigations. The results obtained during this repetition were quite similar to those already published (*loc. cit.*), so that no further mention of them is necessary.

It must, however, be said at once that the data given for ethyl-propylcarbinol must be accepted with reserve, as in spite of a very large amount of laborious work, detailed in another paragraph, there is no certainty that the resolution has been carried to completion.

*The Resolution of Ethyl-*n*-propylcarbinol.*

The resolution of this carbinol has already been described in Part IV. of this series (T., 1913, 103, 1942). It is there stated that the *l*-carbinol was obtained from the more insoluble portion of the brucine salt of the hydrogen phthalic ester, and the *d*-carbinol from the more insoluble portion of the strychnine salt of the hydrogen phthalic ester. The hydrogen phthalates thus obtained had $[\alpha]_D -4.12^\circ$, $+4.18^\circ$, and -3.75° , $+3.77^\circ$ in chloroform and ethyl alcohol respectively.

On repeating this resolution with some fresh *dl*-hydrogen phthalic ester, it was found that the brucine salt behaved in a very erratic manner; the filtrates from the numerous crystalline crops of salt were decomposed, and yielded hydrogen phthalic esters, the rotations of which varied in a very irregular manner from $[\alpha]_D -1.9^\circ$ to $+6.0^\circ$ in alcohol, whilst the brucine salt, which had been crystallised five times successively from acetone, gave a hydrogen phthalate which had $[\alpha]_D$ only -2.3° in ethyl alcohol. This same brucine salt, after seven more crystallisations, gave a hydrogen phthalate, the rotation of which was exactly the same. It thus appears that the most insoluble brucine salt yields a *l*-hydrogen phthalic ester not free from racemate. The above

resolution was carried out in a manner which was believed to be quite similar to the one previously described (*loc. cit.*), and since the initial *dl*-hydrogen phthalic ester gave a correct titration value and had the same melting point as the previously described compound, no explanation of this peculiar behaviour can at present be given. The strychnine salt, on the other hand, behaved similarly to the previously described salt (*loc. cit.*), but on increasing the number of crystallisations gave a *d*-hydrogen phthalic ester of higher rotation than that previously published, namely, $[\alpha]_D + 6.0^\circ$ in ethyl-alcoholic solution. This resolution was again carried out with fresh material, using this time methyl instead of ethyl alcohol as solvent, and again a hydrogen phthalic ester of $[\alpha]_D + 6.0^\circ$ was obtained.

In order to make more sure that this time the resolution was complete, the *quinidine* salt was prepared. This forms fine, silky needles, which readily separate out from acetone. After five or six crystallisations from acetone the salt was obtained with a constant rotation (given below); it was then decomposed in the usual way, and a hydrogen phthalate was obtained with a rotation ($[\alpha]_D - 7.49^\circ$) a little higher than that possessed by the *d*-hydrogen phthalate from the strychnine salt. It was then distilled in a current of steam from excess of sodium hydroxide, and the carbinol thus obtained was used for preparing the acetate and heptoate described in this paper. The following are the data for this resolution.

TABLE I.

Strychnine Salt of d-Ethyl-n-propylcarbinyl Hydrogen Phthalate,
m. p. 191—192°.

Solvent.*	Length of tube. cm.	Wt. of solute. Grams.	α_D	α_{25}	α_{45}
Chloroform	22	1.1093	-2.81°	-3.55°	-7.67°
	$[\alpha]_D$	$[\alpha]_{25}$	$[\alpha]_{45}$	$[M]_D$	$[M]_{25}$
	23.03°	29.10°	62.88°	134.5°	169.9°

Quinidine Salt of l-Ethyl-n-propylcarbinyl Hydrogen Phthalate,
m. p. 161—162°.

Solvent.	Length of tube. cm.	Wt. of solute. Grams.	α_D	α_{25}	α_{45}
Ethyl alcohol	22	1.0416	+14.04°	+16.89°	+31.25°
	$[\alpha]_D$	$[\alpha]_{25}$	$[\alpha]_{45}$	$[M]_D$	$[M]_{25}$
	122.5°	147.3°	272.7°	703.0°	845.7°

* All solutions for the observations of rotatory power recorded in this paper were prepared by making up about 1 gram of the substance to 20 c.c. with the solvent at the temperature of the laboratory, at which temperature all observations were also made.

d-Ethyl-n-propylcarbinyl Hydrogen Phthalate.

Solvent.	Length of tube. cm.	Wt. of solute. Grams.	α_D .	α_{gr} .	α_{vi} .
Ethyl alcohol	22	1.0325	+0.68°	+0.73°	+1.3°
Chloroform	22	1.2350	+0.70	+0.77	+1.49
Carbon disulphide	22	1.0668	+0.45	+0.52	+0.88

	$[\alpha]_D$.	$[\alpha]_{gr}$.	$[\alpha]_{vi}$.	$[M]_D$.	$[M]_{gr}$.	$[M]_{vi}$.
Ethyl alcohol.....	5.99°	6.43°	11.45°	14.97°	16.07°	23.43°
Chloroform	5.15	5.67	10.30	12.88	14.17	25.75
Carbon disulphide..	3.83	4.43	8.35	9.53	11.03	20.87

l-Ethyl-n-propylcarbinyl Hydrogen Phthalate.

Solute.	Length of tube. cm.	Wt. of solute. Grams.	α_D .	α_{gr} .	α_{vi} .
Ethyl alcohol	22	0.9403	-0.75°	—	—
Chloroform	22	1.0410	-0.66	-0.76°	-1.33

	$[\alpha]_D$.	$[\alpha]_{gr}$.	$[\alpha]_{vi}$.	$[M]_D$.	$[M]_{gr}$.	$[M]_{vi}$.
Ethyl alcohol.....	-7.26°	—	—	18.15°	—	—
Chloroform	-5.76	-6.64°	-11.79°	-14.41	-16.59°	-24.47

TABLE II.

l-Ethyl-n-propylcarbinol. Observed Rotations ($\alpha_{165\text{ mm.}}$).

temp.	21°	59°	88°	107°	124°
α_D	-3.46°	-3.52°	-3.60°	-3.60°	-3.64
temp.	21°	50°	89°	107°	124°
α_{gr}	-4.10°	-4.14°	-4.20°	-4.12°	-4.14°
temp.	21°	52°	90°	107°	124°
α_{vi}	-6.80°	-6.94°	-7.00°	-6.90°	-7.09°

Ethyl-n-butylcarbinol.

The resolution of this carbinol was carried out again, and the results were quite similar to those given in Part IV. of this series. The following additional polarimetric determinations were made.

TABLE III.

Strychnine Salt of d-Ethyl-n-butylcarbinyl Hydrogen Phthalate.

Solvent.	Length of tube. cm.	Wt. of solute. Grams.	α_D .	α_{gr} .	α_{vi} .
Ethyl alcohol	22	0.9290	-1.52°	-1.91°	-4.26°

	$[\alpha]_D$.	$[\alpha]_{gr}$.	$[\alpha]_{vi}$.	$[M]_D$.	$[M]_{gr}$.	$[M]_{vi}$.
	-14.87°	-18.69°	-41.69°	-88.94°	-111.8°	-249.3°

d-Ethyl-*n*-butylcarbonyl Hydrogen Phthalate.

Solvent.	Length of tube. cm.	Wt. of solute. Grams.	α_D .	α_{gr} .	α_{vi} .	
Ethyl alcohol	22	0.9972	+2.14°	+2.54°	+4.82°	
Chloroform	22	0.9932	+1.61	+1.87	+3.30	
	$[\alpha]_D$.	$[\alpha]_{gr}$.	$[\alpha]_{vi}$.	$[M]_D$.	$[M]_{gr}$.	$[M]_{vi}$.
Ethyl alcohol ...	+19.51°	+23.15°	+43.93°	+51.50°	+61.12°	+116.0°
Chloroform	+16.21	+18.82	+33.23	+42.80	+49.71	+87.72

The carbinol from this hydrogen phthalic ester gave in a 1-dcm. tube

$$\alpha_D^{18} + 6.89°, \quad \alpha_{gr}^{18} + 8.12°, \quad \alpha_{vi}^{18} + 13.30°.$$

A crystalline *quinidine* salt was also obtained, but it was of little value for purposes of resolution, as its rotation changed only very slightly with recrystallisations.

Resolution of γ -Nonanol.

The resolution of γ -nonanol has been described in Part I. of this series of investigations; for the purpose of preparing the esters described in the present communication, the resolution mentioned above has been carried out on a much larger scale. To the hydrogen phthalate of γ -nonanol (1310 grams) dissolved in acetone was added brucine (1965 grams), and the whole heated on a water-bath until solution was complete. On carrying out the fractional crystallisation in the usual way, there was obtained about 550 grams of pure brucine salt. This, on decomposing, yielded 200 grams of pure *d*-hydrogen phthalate, and the latter when hydrolysed gave 100 grams of the pure *d*- γ -nonanol.

The more soluble portions of the brucine salt were decomposed, and the hydrogen phthalate obtained from it was converted into the cinchonidine salt. This latter was submitted to fractional crystallisation from acetone, and there was eventually obtained about 50 grams of the pure *l*- γ -nonanol. The *d*- γ -nonanol in a 2-dcm. tube gave at 18.5° the following figures:

$$\alpha + 13.46° (l=2), \quad \alpha_{gr} + 15.84° (l=2), \quad \alpha_{vi} + 26.04° (l=2),$$

whence

$$[\alpha]_D^{18.5} + 8.14°, \quad [\alpha]_{gr}^{18.5} + 9.60°, \quad [\alpha]_{vi}^{18.5} + 15.75°.$$

Preparation of the Esters.

Of the esters, the acetates, the propionates, and the *n*-butyrates were obtained by using the corresponding acid anhydrides; the

others were prepared by the interaction in pyridine solution of the carbinol and the corresponding acid chloride. The products, after working up in the usual way, were obtained as substances of constant boiling point, and their purity was checked by the determination of their refractive indices and by ascertaining that their rotatory powers had become constant. In Part V., p. 850, it is mentioned that, in the case of the *n*-butyrates there described, several fractional distillations are necessary before the ester possesses a constant rotatory power and a refractive index which fits on the curve when the refractive indices of the series of esters are plotted. It has since been found that the excess of butyric anhydride used in the preparation of these esters is hydrolysed only very slowly, and the most satisfactory method of removing it is to allow the reaction mixture to remain for several days in contact with sodium carbonate solution, the whole being repeatedly shaken vigorously. The same remarks apply, only to a much less extent, to the propionates. At the end of the investigation the whole of the esters were hydrolysed, and the recovered alcohol was found to have an unaltered rotatory power, thus showing that no racemisation had taken place either during the preparation of the esters or in the subsequent heating of them.

n-Heptoates.

Owing to lack of material, the *n*-heptoates of only some of the carbinols were prepared, and these only in small quantities. The boiling points are tabulated below, but the amounts available did not allow of the determination of the refractive indices. The optical purity of these esters was, however, checked by the regeneration of the respective alcohols, which were found to be unaltered in rotatory powers.

With three exceptions, the esters were obtained as clear, colourless liquids possessing only faint odours; γ -nonyl stearate, γ -hexadecyl acetate, and γ -octadecyl acetate each solidified in the ice-box to crystalline masses, which melted, respectively, at 20°, 19°, and 27°. The physical constants of the esters are given in tables IV and V.

TABLE IV.

 Esters of d- γ -Nonanol, $C_2H_5 \cdot CH(O \cdot CO \cdot R) \cdot C_6H_{13}$.

Ester.	Boiling point.	$n_D^{20^\circ}$.	$D_4^{20^\circ}$.	$n - 1/D. M.$	Difference for CH_2 .
Acetate	99°/18 mm.	1.4190	0.8620	90.4	
Propionate	111°/18 "	1.4217	0.8597	98.1	7.7
Butyrate	119°/13 "	1.4245	0.8580	105.9	7.8
Valerate	133°/18 "	1.4267	0.8559	113.6	7.7
Hexoate	145°/15 "	1.4298	0.8558	121.4	7.8
Heptoate	154°/14 "	1.4325	0.8574	129.1	7.7
Octoate	165°/14 "	1.4345	0.8564	137.0	7.9
Nonoate	137°/3.5 "	1.4365	0.8558	144.8	7.8
Decoate	147°/3 "	1.4382	0.8555	152.6	7.7
Undecoate	157°/3 "	1.4394	0.8554	160.3	7.6
Dodecoate	167°/4 "	1.4415	0.8572	167.9	2 \times 7.9
Myristate	183°/2 "	1.4443	0.8580	183.8	2 \times 7.7
Palmitate	196°/2 "	1.4463	0.8560	199.2	2 \times 7.6
Stearate	217°/3 "	1.4479	0.8570	214.3	

TABLE V.

 Acetates of the Series $C_2H_5 \cdot CH(O \cdot CO \cdot CH_3) \cdot R$.

R.	Boiling point.	$n_D^{20^\circ}$.	$D_4^{20^\circ}$.	$n - 1/D. M.$	Difference for CH_2 .
ethyl	111°	1.3877	0.8715	51.6	
ethyl	131	1.3966	0.8712	59.2	7.6
n-Propyl	156–157°	1.4037	0.8672	67.0	7.8
n-Butyl	65°/17 mm.	1.4098	0.8647	74.8	7.8
n-Amyl	*81°/18 "	1.4147	0.8668	82.4	7.6
n-Hexyl	99°/18 "	1.4190	0.8618	90.3	7.9
n-Heptyl	111°/17 "	1.4223	0.8644	97.7	7.4
n-Octyl	125°/18 "	1.4254	0.8634	105.4	7.7
n-Nonyl	143°/20 "	1.4277	0.8602	113.2	7.8
n-Decyl	152°/14 "	1.4295	0.8620	120.6	7.4
n-Undecyl	164°/15 "	1.4324	0.8609	128.5	7.9
n-Dodecyl	178°/18 "	1.4349	0.8602	136.6	8.1
n-Tridecyl	189°/16 "	1.4370	0.8590	144.5	7.9
n-Pentadecyl	166°/3 "	—	0.8600	—	

* Or 189°/768 mm.

TABLE VI.

n-Heptoate of	B. p.	n-Heptoate of	B. p.
d-Butanol	112°/760 mm.	d- γ -Tridecanol	160°/3 mm.
γ -Hexanol	124°/16 "	l- γ -Tetradecanol	167°/2 "
γ -Heptanol	136°/15 "	l- γ -Pentadecanol	178°/3 "
γ -Octanol	153°/18 "	l- γ -Hexadecanol	187°/2.5 "
γ -Nonanol	154°/14 "	l- γ -Octadecanol	212°/5 "

Acetate of d-Ethylamylcarbinol (γ -Octanol).—Schimmel & Co. "Semi-annual Report," April, 1913) have described this compound, which they prepared from the d-alcohol by heating with acetic anhydride and sodium acetate. Although the observed rotation of the alcohol prepared by them, namely, $\alpha_D + 6.43^\circ$, was less

than that ($\alpha_D + 6.79^\circ$) described in Part IV. of this series of communications, yet the acetate prepared from it had $\alpha_D^{20} - 4.76^\circ$, which is higher than that ($\alpha_D^{20} - 3.73^\circ$) possessed by the acetate of the alcohol described in this communication. The preparation has been repeated, but the result is the same; it was noted that Schimmel's acetate was prepared by using sodium acetate and acetic anhydride, whereas the acetate described in the present paper was prepared by the use of the anhydride alone. In order to test whether this had any effect on the rotation of an acetate prepared by the different method, two lots of *d*- β -octanol were esterified with acetic anhydride, one portion having added to it sodium acetate which had been dried at 110° , and the other portion sodium acetate which had been recently fused. The β -octyl acetate from both preparations had the same rotatory power, and this was identical with the rotatory power of the β -octyl acetate described in Part V. of this series, which was prepared by the use of acetic anhydride alone.

Observed Rotations of the Homogeneous Esters.

The rotations of the esters have been observed at different temperatures, ranging from 15° to 200° , in a 50 mm. tube, round which heated mineral oil was caused to circulate by means of a small pump. The temperature at which a given rotation was determined was taken both before and after the polarimetric readings. Three sets of readings were made: (1) with the light from an ordinary sodium vapour flame passing through a solution of potassium dichromate; (2) with the green mercury vapour light; and (3) with the violet mercury vapour light, in the two latter cases a direct-vision spectroscopic eye-piece being used.

TABLE VII.

Specific and Molecular Rotatory Powers of Esters Prepared from d- γ -Nonanol.*

γ -Nonyl Acetate, $C_6H_{13}\cdot CH_2\cdot O\cdot CO\cdot CH_3$.

t° .	D_t .	$[\alpha]_D^{20}$.	$[\alpha]_D^{25}$.	$[\alpha]_D^{30}$.	$[M]_D^{20}$.	$[M]_D^{25}$.	$[M]_D^{30}$.
20°	0.8618	-5.21°	-6.27°	-11.47°	-9.69°	-11.65°	-21.33°
40	0.8441	5.21	6.29	11.43	9.69	11.70	21.25
60	0.8270	5.25	6.34	11.47	9.78	11.79	21.33
80	0.8095	5.26	6.39	11.56	9.79	11.90	21.50
100	0.7921	5.33	6.43	11.68	9.91	12.04	21.73
120	0.7750	5.39	6.58	11.70	10.03	12.24	21.93
140	0.7578	5.47	6.64	11.88	10.18	12.34	22.10
160	0.7405	5.51	6.67	11.98	10.25	12.41	22.30

* Deduced from observations recorded on pp. 2258-2260.

γ -Nonyl Propionate, $C_9H_{18} \cdot CHEt \cdot O \cdot CO \cdot C_2H_5$.

t.	D _D	$[\alpha]_D^{20}$	$[\alpha]_D^{25}$	$[\alpha]_D^{30}$	$[M]_D^{20}$	$[M]_D^{25}$	$[M]_D^{30}$
20°	0.8601	-5.87°	-7.00°	-12.55°	-11.74°	-14.00°	-25.10°
40	0.8439	5.67	6.81	12.27	11.35	13.63	24.54
60	0.8270	5.53	6.67	12.03	11.05	13.35	24.06
80	0.8100	5.43	6.58	11.85	10.87	13.16	23.70
100	0.7930	5.36	6.51	11.70	10.72	13.01	23.40
120	0.7761	5.35	6.40	11.54	10.69	12.81	23.08
140	0.7595	5.30	6.39	11.39	10.60	12.77	22.78
160	0.7427	5.28	6.42	11.27	10.56	12.84	22.54

 γ -Nonyl n-Butyrate, $C_9H_{18} \cdot CHEt \cdot O \cdot CO \cdot C_4H_9$.

t.	D _D	$[\alpha]_D^{20}$	$[\alpha]_D^{25}$	$[\alpha]_D^{30}$	$[M]_D^{20}$	$[M]_D^{25}$	$[M]_D^{30}$
20°	0.8575	-3.38°	-4.11°	-7.59°	-7.24°	-8.79°	-16.25°
40	0.8409	3.31	4.05	7.54	7.07	8.68	16.14
60	0.8243	3.27	4.00	7.49	7.01	8.57	16.03
80	0.8078	3.22	3.96	7.43	6.89	8.48	15.90
100	0.7908	3.20	3.92	7.39	6.85	8.39	15.81
120	0.7734	3.15	3.88	7.34	6.75	8.30	15.70
140	0.7562	3.11	3.83	7.27	6.65	8.21	15.56
160	0.7391	3.06	3.76	7.21	6.54	8.05	15.43
180	0.7221	3.01	3.70	7.13	6.45	7.93	15.26
200	0.7049	2.95	3.62	7.09	6.35	7.74	15.17

 γ -Nonyl n-Valerate, $C_9H_{18} \cdot CHEt \cdot O \cdot CO \cdot C_5H_9$.

t.	D _D	$[\alpha]_D^{20}$	$[\alpha]_D^{25}$	$[\alpha]_D^{30}$	$[M]_D^{20}$	$[M]_D^{25}$	$[M]_D^{30}$
20°	0.8560	-3.12°	-3.85°	-7.18°	-7.11°	-8.79°	-16.38°
40	0.8399	3.01	3.78	6.96	6.85	8.62	15.88
60	0.8234	2.91	3.68	6.79	6.64	8.39	15.47
80	0.8071	2.82	3.57	6.60	6.43	8.13	15.05
100	0.7910	2.73	3.45	6.41	6.23	7.85	14.61
120	0.7747	2.63	3.32	6.19	6.00	7.58	14.13
140	0.7584	2.56	3.20	6.00	5.84	7.29	13.68
160	0.7420	2.49	3.09	5.78	5.68	7.04	13.18
180	0.7258	2.41	2.96	5.55	5.49	6.75	12.65
200	0.7095	2.33	2.80	5.31	5.30	6.39	12.12

 γ -Nonyl n-Hexate, $C_9H_{18} \cdot CHEt \cdot O \cdot CO \cdot C_6H_{11}$.

t.	D _D	$[\alpha]_D^{20}$	$[\alpha]_D^{25}$	$[\alpha]_D^{30}$	$[M]_D^{20}$	$[M]_D^{25}$	$[M]_D^{30}$
20°	0.8556	-2.66°	-3.33°	-6.23°	-6.45°	-8.06°	-15.08°
40	0.8400	2.56	3.21	6.04	6.19	7.78	14.61
60	0.8250	2.43	3.12	5.82	5.89	7.55	14.08
80	0.8089	2.35	3.03	5.62	5.68	7.33	13.61
100	0.7930	2.24	2.90	5.45	5.43	7.02	13.18
120	0.7770	2.16	2.80	5.26	5.23	7.78	12.74
140	0.7611	2.09	2.69	5.06	5.05	6.52	12.24
160	0.7451	2.02	2.55	4.90	4.89	6.17	11.85
180	0.7291	1.95	2.44	4.70	4.71	5.91	11.39
200	0.7134	1.88	2.31	4.56	4.55	5.60	11.03

 γ -Nonyl n-Heptate, $C_9H_{18} \cdot CHEt \cdot O \cdot CO \cdot C_7H_{13}$.

t.	D _D	$[\alpha]_D^{20}$	$[\alpha]_D^{25}$	$[\alpha]_D^{30}$	$[M]_D^{20}$	$[M]_D^{25}$	$[M]_D^{30}$
20°	0.8575	-2.36°	-2.91°	-5.62°	-6.03°	-7.46°	-14.33°
40	0.8416	2.26	2.82	5.39	5.78	7.21	13.81
60	0.8255	2.18	2.70	5.16	5.58	6.91	13.20
80	0.8093	2.10	2.59	4.95	5.37	6.64	12.65
100	0.7932	2.02	2.50	4.79	5.16	6.39	12.26
120	0.7770	1.93	2.39	4.59	4.94	6.13	11.76
140	0.7610	1.84	2.30	4.42	4.71	5.88	11.33
160	0.7445	1.76	2.19	4.23	4.50	5.61	10.82
180	0.7284	1.68	2.09	4.09	4.30	5.36	10.47
200	0.7125	1.59	2.01	3.96	4.06	5.13	10.14

γ-Nonyl n-Octoate, $C_9H_{19} \cdot CHEt \cdot O \cdot CO \cdot C_8H_{17}$.

	D_4^t	$[\alpha]_D^{20}$	$[\alpha]_D^{25}$	$[\alpha]_D^{30}$	$[M]_D^{20}$	$[M]_D^{25}$	$[M]_D^{30}$
20°	0.8566	-2.10°	-2.64°	-4.94°	-5.67°	-6.87°	-13.33°
40	0.8414	2.02	2.50	4.81	5.45	6.74	13.60
60	0.8260	1.94	2.42	4.66	5.23	6.54	13.59
80	0.8100	1.85	2.35	4.54	5.00	6.33	13.27
100	0.7941	1.76	2.28	4.39	4.76	6.15	11.87
120	0.7782	1.66	2.20	4.24	4.48	5.93	11.45
140	0.7625	1.55	2.12	4.06	4.18	5.74	10.97
160	0.7468	1.43	2.03	3.91	3.87	5.49	10.55
180	0.7312	1.33	1.95	3.73	3.68	5.28	10.08
200	0.7155	1.20	1.87	3.56	3.24	5.06	9.62

γ-Nonyl n-Nonoate, $C_9H_{19} \cdot CHEt \cdot O \cdot CO \cdot C_9H_{17}$.

	D_4^t	$[\alpha]_D^{20}$	$[\alpha]_D^{25}$	$[\alpha]_D^{30}$	$[M]_D^{20}$	$[M]_D^{25}$	$[M]_D^{30}$
20°	0.8560	-1.94°	-2.45°	-4.59°	-5.50°	-6.97°	-13.06°
40	0.8410	1.84	2.38	4.46	5.23	6.75	12.67
60	0.8260	1.76	2.29	4.33	4.99	6.50	12.29
80	0.8114	1.68	2.22	4.21	4.76	6.30	11.97
100	0.7965	1.59	2.11	4.08	4.53	5.99	11.59
120	0.7815	1.48	2.02	3.94	4.22	5.74	11.19
140	0.7668	1.37	1.93	3.79	3.89	5.48	10.77
160	0.7518	1.26	1.83	3.66	3.69	5.19	10.39
180	0.7370	1.15	1.74	3.49	3.27	4.93	9.92
200	0.7220	1.04	1.63	3.31	2.95	4.62	9.40

γ-Nonyl n-Decoate, $C_9H_{19} \cdot CHEt \cdot O \cdot CO \cdot C_{10}H_{21}$.

	D_4^t	$[\alpha]_D^{20}$	$[\alpha]_D^{25}$	$[\alpha]_D^{30}$	$[M]_D^{20}$	$[M]_D^{25}$	$[M]_D^{30}$
20°	0.8555	-1.90°	-2.44°	-4.33°	-5.68°	-7.28°	-13.06°
40	0.8405	1.84	2.38	4.28	5.49	7.09	12.77
60	0.8258	1.78	2.31	4.18	5.30	6.89	12.45
80	0.8107	1.73	2.24	4.07	5.14	6.69	12.13
100	0.7958	1.66	2.16	3.96	4.94	6.44	11.80
120	0.7810	1.57	2.05	3.84	4.69	6.10	11.45
140	0.7658	1.50	1.96	3.72	4.47	5.83	11.09
160	0.7506	1.41	1.86	3.60	4.21	5.56	10.72
180	0.7358	1.32	1.77	3.46	3.93	5.26	10.32
200	0.7210	1.25	1.66	3.33	3.72	4.96	9.92

γ-Nonyl n-Undecoate, $C_9H_{19} \cdot CHEt \cdot O \cdot CO \cdot C_{11}H_{23}$.

	D_4^t	$[\alpha]_D^{20}$	$[\alpha]_D^{25}$	$[\alpha]_D^{30}$	$[M]_D^{20}$	$[M]_D^{25}$	$[M]_D^{30}$
20°	0.8543	-1.83°	-2.28°	-4.33°	-5.70°	-7.12°	-13.51
40	0.8402	1.79	2.24	4.25	5.58	6.98	13.26
60	0.8254	1.76	2.19	4.12	5.48	6.84	12.85
80	0.8106	1.70	2.11	3.91	5.31	6.58	12.20
100	0.7950	1.61	2.01	3.71	5.02	6.28	11.58
120	0.7801	1.51	1.89	3.46	4.70	5.90	10.80
140	0.7656	1.42	1.80	3.29	4.44	5.61	10.28
160	0.7509	1.33	1.69	3.08	4.15	4.28	9.60
180	0.7361	1.22	1.59	2.87	3.82	4.96	8.94
200	0.7214	1.11	1.45	2.63	3.46	4.54	8.22

γ -Nonyl n-Dodecoate, $C_6H_{13} \cdot CHEt \cdot O \cdot CO \cdot C_{11}H_{23}$.

t.	D _t	[α] _D ^t	[α] _D ^t	[α] _D ^t	[M] _D ^t	[M] _D ^t	[M] _D ^t
		-1.63°	-2.08°	-3.85°	-5.32°	-6.77°	-12.54°
20°	0.8573						
40	0.8430	1.55	1.99	3.71	5.07	6.50	12.09
60	0.8287	1.48	1.93	3.67	4.84	6.29	11.64
80	0.8144	1.41	1.84	3.43	4.60	6.00	11.18
100	0.8000	1.34	1.75	3.27	4.38	5.70	10.68
120	0.7856	1.27	1.68	3.12	4.15	5.48	10.16
140	0.7714	1.21	1.59	2.94	3.93	5.18	9.59
160	0.7570	1.12	1.49	2.77	3.66	4.87	9.04
180	0.7429	0.99	1.39	2.58	3.23	4.52	8.42
200	0.7287	0.96	1.29	2.39	3.13	4.21	7.78

 γ -Nonyl Myristate, $C_6H_{13} \cdot CHEt \cdot O \cdot CO \cdot C_{13}H_{27}$.

t.	D _t	[α] _D ^t	[α] _D ^t	[α] _D ^t	[M] _D ^t	[M] _D ^t	[M] _D ^t
		-1.55°	-2.01°	-3.74°	-5.50°	-7.11°	-13.23°
20°	0.8560						
40	0.8427	1.51	1.94	3.61	5.33	6.89	12.77
60	0.8282	1.47	1.87	3.46	5.21	6.62	12.27
80	0.8134	1.43	1.81	3.34	5.05	6.40	11.84
100	0.7989	1.34	1.73	3.19	4.85	6.11	11.30
120	0.7843	1.27	1.64	3.03	4.51	5.82	10.74
140	0.7699	1.21	1.56	2.87	4.28	5.52	10.16
160	0.7554	1.15	1.48	2.71	4.08	5.25	9.61
180	0.7410	1.08	1.39	2.54	3.82	4.92	8.98
200	0.7260	0.99	1.28	2.34	3.51	4.53	8.29

 γ -Nonyl Palmitate, $C_6H_{13} \cdot CHEt \cdot O \cdot CO \cdot C_{15}H_{31}$.

t.	D _t	[α] _D ^t	[α] _D ^t	[α] _D ^t	[M] _D ^t	[M] _D ^t	[M] _D ^t
		-1.49°	-1.86°	-3.34°	-5.71°	-7.10°	-12.77°
20°	0.8560						
40	0.8418	1.46	1.80	3.27	5.58	6.89	12.48
60	0.8274	1.43	1.75	3.20	5.45	6.70	12.24
80	0.8130	1.39	1.67	3.11	5.31	6.39	11.94
100	0.7986	1.34	1.60	3.00	5.12	6.12	11.48
120	0.7847	1.30	1.55	2.93	4.97	5.94	11.19
140	0.7709	1.23	1.49	2.82	4.71	5.70	10.77
160	0.7560	1.16	1.39	2.71	4.45	5.31	10.36
180	0.7415	1.08	1.28	2.57	4.12	4.89	9.84
200	0.7270	0.96	1.17	2.45	3.68	4.47	9.35

 γ -Nonyl Stearate, $C_6H_{13} \cdot CHEt \cdot O \cdot CO \cdot C_{17}H_{35}$.

t.	D _t	[α] _D ^t	[α] _D ^t	[α] _D ^t	[M] _D ^t	[M] _D ^t	[M] _D ^t
		-1.49°	-1.78°	-3.17°	-6.12°	-7.31°	-13.02°
20°	0.8572						
40	0.8430	1.46	1.74	3.08	5.98	7.15	12.65
60	0.8289	1.43	1.71	3.00	5.88	7.02	12.31
80	0.8148	1.39	1.67	2.92	5.69	6.84	11.98
100	0.8005	1.34	1.62	2.85	5.48	6.66	11.68
120	0.7861	1.30	1.59	2.76	5.32	6.52	11.32
140	0.7728	1.25	1.53	2.65	5.14	6.26	10.88
160	0.7582	1.20	1.46	2.57	4.92	6.00	10.54
180	0.7444	1.14	1.41	2.46	4.68	5.78	10.08
200	0.7302	1.10	1.37	2.37	4.49	5.62	9.71

TABLE VIII.
*Determination of Rotatory Power of Esters of d-γ-Nonanol in (approximately) 5 per cent.
 Ethyl-alcoholic Solution.*

Ester.	Weight of substance in grams.	Length of tube in cm.	α_D^{20}	α_D^{25}	α_D^{30}	α_D^{35}	$[\alpha]_D^{20}$	$[\alpha]_D^{25}$	$[\alpha]_D^{30}$	$[\alpha]_D^{35}$	$[\alpha]_D^{40}$	$[\alpha]_D^{45}$
Acetate	0.8988	20	-0.73°	-0.86°	+1.62°	-8.12°	-9.57°	-10.90°	-13.10°	-17.79°	-31.46°	-31.46°
Propionate	1.0475	22	1.01	1.23	2.07	8.77	10.68	17.97	17.64	21.36	35.94	35.94
n-Butyrate	1.0386	"	0.65	0.76	1.32	5.69	6.65	11.55	12.17	14.23	24.73	24.73
n-Valerate	1.0194	20	0.50	0.57	0.98	4.91	5.59	9.61	11.19	12.75	21.92	21.92
n-Hexanoate	0.9767	22	0.45	0.53	0.95	4.19	4.93	8.84	10.14	11.94	21.40	21.40
n-Heptanoate	1.0341	"	0.39	0.46	0.81	3.67	4.32	7.61	9.39	11.04	19.49	19.49
n-Octanoate	1.0070	"	0.34	0.39	0.67	3.07	3.52	6.05	8.29	9.51	16.33	16.33
n-Nonanoate	1.0521	20	0.29	0.35	0.57	2.76	3.48	5.42	7.83	9.89	15.39	15.39
n-Decanoate	1.1440	22	0.30	0.38	0.69	2.62	3.32	6.03	7.81	9.90	17.97	17.97
n-Undecanoate	1.0882	"	0.29	0.34	0.63	2.42	2.84	5.26	7.56	8.87	16.43	16.43
n-Dodecanoate	1.0175	"	0.27	0.32	0.50	2.36	2.86	4.47	7.68	9.32	14.66	14.66
Myristate	—	"	0.27	0.29	0.45	2.31	2.48	3.85	8.17	8.78	13.62	13.62
Palmitate	0.9465	"	0.25	0.28	0.35	2.40	2.69	3.36	9.17	10.28	12.84	12.84
Stearate	0.9505	"	0.24	0.26	0.39	2.30	2.49	3.33	9.41	10.20	13.63	13.63

All the rotations recorded above are levorotatory.

TABLE IX.

Determination of Rotatory Power of Esters of d-γ-Nonanol in (approximately) 5 per cent. Carbon Disulphide Solution.

Ester.	Weight of Lanthanum salt, in gms.	α_D^{20}	α_D^{25}	α_D^{30}	$[\alpha]_D^{20}$	$[\alpha]_D^{25}$	$[\alpha]_D^{30}$	$[\eta]_{inh}^{25}$	$[\eta]_{inh}^{30}$	$[\eta]_{inh}^{35}$
Acetate	1.0228	20	-1.83°	-2.18°	-3.95°	-17.90°	-21.31°	-38.62°	-33.29°	-39.86°
Propionate	1.0800	"	2.25	2.07	4.78	20.72	25.59	44.01	41.44	51.18
n-Butyrate	1.0350	"	1.77	2.12	3.80	17.10	24.80	36.74	36.60	43.83
n-Pentanoate	1.0095	"	1.65	1.96	3.48	15.36	19.42	34.48	34.01	48.81
n-Hexanoate	1.0508	"	1.53	1.84	3.31	14.55	17.51	31.49	35.23	42.36
n-Heptanoate	1.0007	"	1.34	1.61	2.83	13.40	16.10	28.30	34.30	41.21
n-Octanoate	1.0868	"	1.36	1.67	2.85	12.51	15.37	26.22	33.78	41.49
n-Nonanoate	1.0591	"	1.23	1.56	2.64	11.90	14.73	24.93	33.50	41.83
n-Decanoate	1.1438	"	1.23	1.56	2.75	10.75	13.93	24.04	32.04	40.63
n-Undecanoate	1.1494	"	1.19	1.45	2.68	10.35	12.61	23.31	32.29	39.36
n-Dodecanoate	0.9980	"	1.03	1.25	2.20	10.30	12.51	22.02	33.60	40.79
Myristate	0.9848	"	0.96	1.15	2.00	9.75	11.68	20.31	34.60	41.88
Palmitate	1.0276	"	0.94	1.08	1.93	9.15	10.51	18.78	34.94	40.15
Stearate	1.0487	"	0.91	1.10	1.88	8.67	10.49	17.93	35.54	43.01

All the rotations recorded above are levorotatory.

TABLE X.
Determination of Rotatory Power of d-γ-Nonanol in Various Solvents at the Temperature of the Laboratory.

Solvent.	Weight of solute in grams.	Length of tube in cm.	α_D^{20}	α_D^{19}	α_D^{18}	$[\alpha]_D^{20}$	$[\alpha]_D^{19}$	$[\alpha]_D^{18}$	$[\alpha]_D^{17}$	$[\alpha]_D^{16}$	$[\alpha]_D^{15}$	$[\alpha]_D^{14}$	$[\alpha]_D^{13}$	$[\alpha]_D^{12}$	$[\alpha]_D^{11}$	$[\alpha]_D^{10}$	$[\alpha]_D^9$	$[\alpha]_D^8$	$[\alpha]_D^7$	$[\alpha]_D^6$	$[\alpha]_D^5$	$[\alpha]_D^4$	$[\alpha]_D^3$	$[\alpha]_D^2$	$[\alpha]_D^1$	$[\alpha]_D^0$
Benzene	1.0734	20	+1.00°	+1.19°	+1.99°	+9.32°	+11.09°	+18.55°	+13.42°	+16.97°	+26.71°	+26.04														
Chloroform	1.1395	"	1.02	1.21	2.06	8.95	10.62	18.08	12.89	15.30	26.04															
Ethyl alcohol	1.0595	"	0.95	1.09	1.85	9.16	10.29	17.47	13.19	14.82	25.16															
Ethyl acetate	1.0543	22	1.04	1.18	1.99	8.97	10.18	17.17	12.92	14.66	24.73															
Carbon disulphide	1.0842	"	0.96	1.11	1.89	8.05	9.31	15.85	11.80	13.41	22.83															
Pyridine	1.1117	20	0.54	0.67	1.01	4.86	6.03	9.08	6.99	8.68	13.08															

TABLE XI.
Determination of Rotatory Power of Acetate of d-γ-Nonanol in Various Solvents at the Temperature of the Laboratory.

Solvent.	Weight of solute in grams.	Length of tube in cm.	α_D^{20}	α_D^{19}	α_D^{18}	$[\alpha]_D^{20}$	$[\alpha]_D^{19}$	$[\alpha]_D^{18}$	$[\alpha]_D^{17}$	$[\alpha]_D^{16}$	$[\alpha]_D^{15}$	$[\alpha]_D^{14}$	$[\alpha]_D^{13}$	$[\alpha]_D^{12}$	$[\alpha]_D^{11}$	$[\alpha]_D^{10}$	$[\alpha]_D^9$	$[\alpha]_D^8$	$[\alpha]_D^7$	$[\alpha]_D^6$	$[\alpha]_D^5$	$[\alpha]_D^4$	$[\alpha]_D^3$	$[\alpha]_D^2$	$[\alpha]_D^1$	$[\alpha]_D^0$
Pyridine	0.9641	20	-1.29°	-1.55°	-2.48°	-13.39°	-16.08°	-25.72°	-24.39°	-29.90°	-47.55°															
Benzene	0.9683	22	1.32	1.58	2.71	12.42	14.87	26.50	23.10	27.65	47.42															
Chloroform	0.9230	"	0.84	0.97	1.65	8.73	9.55	16.25	15.39	17.77	30.23															
Ethyl acetate	0.9992	20	0.59	0.70	1.22	6.91	7.00	12.21	10.98	13.03	22.71															
Acetone	0.9374	"	0.57	0.67	1.13	6.08	7.15	12.00	11.31	13.29	22.48															
Ethylene dibromide	0.9796	22	0.40	0.48	0.87	3.74	4.49	8.13	6.53	8.34	15.12															

The rotations recorded in Table XI are all involuntary.

TABLE XII.

Specific and Molecular Rotatory Powers of the Acetates derived from the Carbinols of the Formula $C_2H_5 \cdot CH(OH) \cdot R$.*

Acetate of d-γ-Hexanol, $C_2H_5 \cdot CH(O \cdot CO \cdot CH_3) \cdot C_6H_{13}$.

t.	D_D^t	$[\alpha]_D^{20}$	$[\alpha]_D^{25}$	$[\alpha]_D^{30}$	$[M]_D^{20}$	$[M]_D^{25}$	$[M]_D^{30}$
20°	0.8677	+0.55°	+0.65°	+0.71°	+0.79°	+0.93°	+1.03°
40	0.8480	0.54	0.63	0.70	0.78	0.91	1.00
60	0.8287	0.52	0.61	0.68	0.75	0.89	0.99
80	0.8082	0.51	0.60	0.67	0.73	0.86	0.96
100	0.7885	0.50	0.58	0.65	0.71	0.83	0.94
120	0.7688	0.48	0.56	0.63	0.69	0.80	0.91
140	0.7490	0.46	0.54	0.61	0.66	0.77	0.88

Acetate of d-γ-Heptanol, $C_2H_5 \cdot CH(O \cdot CO \cdot CH_3) \cdot C_7H_{15}$.

20°	0.8649	-4.68°	-5.66°	-10.44°	-7.40°	-8.95°	-16.47°
40	0.8458	4.73	5.73	10.62	7.47	9.06	16.63
60	0.8267	4.78	5.80	10.63	7.55	9.17	16.80
80	0.8080	4.83	5.88	10.73	7.63	9.29	16.95
100	0.7890	4.88	5.94	10.83	7.71	9.39	17.12
120	0.7700	4.93	6.01	10.95	7.80	9.50	17.30
140	0.7510	4.98	6.08	11.07	7.87	9.62	17.49
160	0.7320	5.03	6.16	11.20	7.94	9.74	17.70

Acetate of d-γ-Octanol, $C_2H_5 \cdot CH(O \cdot CO \cdot CH_3) \cdot C_8H_{17}$.

20°	0.8670	-4.30°	-5.03°	-9.63°	-7.40°	-8.73°	-16.57°
40	0.8489	4.37	5.15	9.75	7.52	8.85	16.77
60	0.8300	4.46	5.24	9.88	7.54	9.01	16.99
80	0.8110	4.54	5.34	10.02	7.80	9.18	17.24
100	0.7920	4.61	5.43	10.16	7.93	9.34	17.48
120	0.7722	4.71	5.54	10.30	8.12	9.53	17.71
140	0.7546	4.77	5.63	10.43	8.21	9.69	17.94
160	0.7359	4.86	5.73	10.59	8.37	9.86	18.21
180	0.7174	4.96	5.85	10.74	8.53	10.07	18.46

† Acetate of l-γ-Decanol, $C_2H_5 \cdot CH(O \cdot CO \cdot CH_3) \cdot C_{10}H_{21}$.

20°	0.8642	+4.48°	+5.40°	+9.85°	+9.96°	+10.80°	+19.70°
40	0.8472	4.53	5.44	9.91	9.06	10.88	19.82
60	0.8299	4.56	5.48	9.96	9.12	10.96	19.92
80	0.8120	4.62	5.53	10.03	9.24	11.06	20.06
100	0.7940	4.66	5.57	10.10	9.32	11.14	20.20
120	0.7760	4.72	5.61	10.20	9.44	11.22	20.40
140	0.7580	4.77	5.67	10.29	9.54	11.34	20.58
160	0.7405	4.82	5.70	10.40	9.64	11.40	20.80
180	0.7229	4.87	5.74	10.49	9.74	11.48	20.98
200	0.7051	4.92	5.79	10.59	9.84	11.58	21.18

* Deduced from data recorded on pp. 2260, 2261

† See table VII for acetate of d-γ-nonanol.

Acetate of 1-γ-Undecanol, C₂H₅·CH(O·CO·CH₃)·C₉H₁₇.

t°.	D _t ^t	[α] _D ^t	[α] _D ^t _{gr.}	[α] _D ^t _{liq.}	[M] _D ^t	[M] _D ^t _{gr.}	[M] _D ^t _{liq.}
20°	0.8635	+4.40°	+5.11°	+9.38°	+9.42°	+10.92°	+20.01°
40	0.8478	4.40	5.14	9.44	9.41	11.02	20.19
60	0.8310	4.42	5.20	9.49	9.45	11.13	20.22
80	0.8133	4.45	5.24	9.55	9.52	11.20	20.44
100	0.7954	4.47	5.28	9.62	9.58	11.30	20.63
120	0.7780	4.50	5.33	9.69	9.63	11.41	20.74
140	0.7610	4.53	5.37	9.72	9.70	11.50	20.81
160	0.7439	4.57	5.35	9.80	9.78	11.45	21.60
180	0.7268	4.58	5.48	9.88	9.80	11.72	21.13
200	0.7096	4.59	5.40	9.95	9.83	11.55	21.30

Acetate of 1-γ-Dodecanol, C₂H₅·CH(O·CO·CH₃)·C₉H₁₉.

t°	D _t	+3.68°	+4.43°	+8.14°	+8.40°	+10.06°	+18.56°
20°	0.8602						
40	0.8452	3.64	4.38	8.04	8.31	9.98	18.33
60	0.8298	3.59	4.31	7.98	8.19	9.83	18.22
80	0.8132	3.57	4.28	7.93	8.13	9.76	18.08
100	0.7968	3.55	4.24	7.88	8.10	9.67	17.97
120	0.7799	3.59	4.23	7.89	8.19	9.65	17.99
140	0.7632	3.63	4.26	7.97	8.27	9.71	18.18
160	0.7470	3.71	4.28	8.05	8.45	9.77	18.35
180	0.7310	3.80	4.31	8.19	8.66	9.83	18.67
200	0.7149	3.85	4.36	8.37	8.77	9.95	19.08

Acetate of 1-γ-Tridecanol, C₂H₅·CH(O·CO·CH₃)·C₁₀H₁₉.

t°	D _t	+3.83°	+4.61°	+8.49°	+9.26°	+11.20°	+20.55°
20°	0.8620						
40	0.8470	3.86	4.64	8.53	9.34	11.23	20.63
60	0.8320	3.90	4.69	8.56	9.45	11.34	20.71
80	0.8160	3.93	4.71	8.60	9.52	11.40	20.82
100	0.7995	3.97	4.73	8.66	9.60	11.44	20.94
120	0.7825	4.00	4.75	8.72	9.68	11.50	21.10
140	0.7635	4.03	4.78	8.78	9.76	11.60	21.23
160	0.7420	4.08	4.84	8.89	9.88	11.70	21.52
180	0.7190	4.13	4.91	9.03	10.00	11.90	21.84
200	0.6980	4.17	4.94	9.14	10.10	12.00	22.12

Acetate of 1-γ-Tetradecanol, C₂H₅·CH(O·CO·CH₃)·C₁₁H₂₃.

t°	D _t	+3.69°	+4.44°	+8.17°	+9.45°	+11.36°	+20.90°
20°	0.8610						
40	0.8457	3.70	4.46	8.22	9.47	11.41	21.03
60	0.8307	3.73	4.49	8.27	9.55	11.49	21.16
80	0.8154	3.76	4.51	8.33	9.64	11.55	21.31
100	0.7999	3.79	4.56	8.38	9.70	11.63	21.44
120	0.7850	3.82	4.58	8.44	9.78	11.74	21.62
140	0.7699	3.86	4.61	8.52	9.88	11.80	21.81
160	0.7545	3.91	4.64	8.59	10.01	11.88	21.99
180	0.7395	3.95	4.68	8.66	10.11	11.98	22.16
200	0.7243	3.99	4.71	8.75	10.22	12.05	22.39

Acetate of 1-γ-Pentadecanol, C₂H₅·CH(O·CO·CH₃)·C₁₂H₂₅

<i>t</i> .	D _c .	[α] _D ^c .	[α] ₅₇₈ ^c .	[α] ₅₇₈ ^t .	[M] _D ^c .	[M] ₅₇₈ ^c .	[M] ₅₇₈ ^t .
20°	0.8601	+3.63°	+4.42°	+8.08°	+9.95°	+11.93°	+21.82°
40	0.8455	3.67	4.42	8.10	9.90	11.94	21.83
60	0.8308	3.68	4.43	8.12	9.94	11.96	21.94
80	0.8158	3.69	4.45	8.15	9.96	12.01	22.01
100	0.8010	3.70	4.47	8.18	9.98	12.07	22.08
120	0.7859	3.70	4.49	8.21	10.00	12.13	22.16
140	0.7710	3.70	4.51	8.23	9.98	12.19	22.24
160	0.7556	3.71	4.53	8.30	10.01	12.23	22.42
180	0.7410	3.71	4.52	8.37	10.02	12.21	22.59
200	0.7260	3.71	4.56	8.40	10.01	12.27	22.69

Acetate of 1-γ-Hexadecanol, C₂H₅·CH(O·CO·CH₃)·C₁₃H₂₇

<i>t</i> .	D _c .	[α] _D ^c .	[α] ₅₇₈ ^c .	[α] ₅₇₈ ^t .	[M] _D ^c .	[M] ₅₇₈ ^c .	[M] ₅₇₈ ^t .
20°	0.8500	+3.19°	+3.86°	+7.2	+9.06°	+11.00°	+20.6°
40	0.8447	3.21	3.87	7.25	9.11	11.00	20.6
60	0.8300	3.24	3.89	7.28	9.20	11.05	20.7
80	0.8148	3.26	3.89	7.30	9.27	11.05	20.74
100	0.7993	3.31	3.90	7.35	9.41	11.10	20.89
120	0.7847	3.35	3.91	7.39	9.52	11.11	20.99
140	0.7701	3.38	3.92	7.44	9.59	11.14	21.13
160	0.7552	3.40	3.93	7.50	9.66	11.17	21.28
180	0.7408	3.44	3.97	7.59	9.77	11.27	21.54
200	0.7259	3.47	4.00	7.69	9.86	11.34	21.83

Acetate of 1-γ-Octadecanol, C₂H₅·CH(O·CO·CH₃)·C₁₅H₃₁

<i>t</i> .	D _c .	[α] _D ^c .	[α] ₅₇₈ ^c .	[α] ₅₇₈ ^t .	[M] _D ^c .	[M] ₅₇₈ ^c .	[M] ₅₇₈ ^t .
20°	0.8600	+2.98°	+3.72°	+6.63°	+9.28°	+11.61°	+20.63°
40	0.8448	3.01	3.53	6.65	9.38	11.01	20.76
60	0.8317	3.00	3.53	6.67	9.38	10.92	20.82
80	0.8172	3.02	3.55	6.71	9.43	11.08	20.92
100	0.8028	3.05	3.56	6.75	9.52	11.12	21.07
120	0.7880	3.06	3.58	6.79	9.54	11.16	21.18
140	0.7732	3.08	3.58	6.85	9.60	11.19	21.39
160	0.7587	3.11	3.60	6.89	9.70	11.23	21.51
180	0.7442	3.14	3.63	6.93	9.81	11.32	21.63
200	0.7298	3.16	3.63	6.99	9.88	11.33	21.81

TABLE XIII.
Determination of Rotatory Powers of the Acetates in (approx.) 5 per cent. Ethyl-alcoholic Solution.

Acetate of	Length of tube, cm.	Weight of solute, Grams.	α_D^{20}	α_D^{25}	α_D^{30}	$[\alpha]_D^{25}$	$[\alpha]_D^{30}$	$[\alpha]_D^{35}$	$[\alpha]_D^{40}$	$[\alpha]_D^{45}$	$[\alpha]_D^{50}$
<i>d</i> - β Butanol	20	1.0048	+2.60°	+3.06°	+5.03°	+25.87°	+30.45°	+50.06°	+30.41°	+35.32°	+58.07°
γ -Pentanol		Inactive									
<i>d</i> - γ Hexanol	22	1.0669	-0.04	-0.05	-0.07	-0.34	-0.43	-0.50	-0.49	-0.62	-0.86
<i>d</i> - γ Heptanol	"	1.0563	-0.93	-1.04	-1.89	-8.01	-8.96	-16.28	-12.66	-14.15	-25.72
<i>d</i> - γ Octanol	"	1.0671	-0.87	-1.02	-1.81	-7.41	-8.69	-15.42	-12.76	-14.95	-26.53
<i>d</i> - γ Nonanol	20	0.9988	-0.73	-0.86	-1.52	-8.12	-9.37	-16.90	-15.10	-17.79	-31.45
<i>l</i> - γ Decanol	22	1.0564	+0.84	+1.03	+1.81	+7.24	+8.87	+15.58	+14.47	+17.73	+31.17
<i>l</i> - γ Undecanol	"	1.0221	+0.80	+0.95	+1.67	+7.12	+8.45	+14.86	+15.23	+18.08	+31.78
<i>l</i> - γ Dodecanol	20	0.9968	+0.60	+0.74	+1.36	+6.02	+7.42	+13.64	+13.73	+17.32	+31.11
<i>l</i> - γ Tridecanol	22	1.0879	+0.81	+0.98	+1.73	+6.77	+8.19	+14.46	+16.38	+19.82	+34.99
<i>l</i> - γ Tetradecanol ..	"	1.1543	+0.85	+1.03	+1.90	+6.89	+8.11	+14.97	+17.15	+20.77	+38.32
<i>l</i> - γ Pentadecanol ...	20	1.1082	+0.73	+0.92	+1.67	+6.61	+8.31	+15.08	+17.79	+22.43	+40.70
<i>l</i> - γ Hexadecanol ...	22	1.1245	+0.81	+0.94	+1.64	+6.56	+7.60	+13.27	+18.63	+21.59	+37.67
<i>l</i> - γ Octadecanol ...	20	1.2741	+0.76	+0.90	+1.56	+5.96	+7.05	+12.25	+18.61	+22.04	+38.20

TABLE XIV.
Determinations of Rotatory Powers of the Acetates derived from the Carbinols of the Formula $C_2H_5 \cdot CH(OH) \cdot R$ in (approx.) 5 per cent. Carbon Disulphide Solution.

Acetate of solute, tube.	Weight of of Grams. cm.	α_D^{20}	α_D^{164}	α_D^{192}	α_D^{239}	$[\alpha]_D^{20}$	$[\alpha]_D^{164}$	$[\alpha]_D^{192}$	$[\alpha]_D^{239}$	$[M]_D^{1812}$	$[M]_D^{2124}$	$[M]_D^{3193}$
<i>d</i> -Ethylmethylcarbinol	1.0496	20	+1.64°	+1.92°	+2.39°	+15.62°	+18.31°	+27.53°	+18.12°	+21.24°	+31.93°	
Diethylcarbinol	Inactive											
<i>d</i> -Ethyl- <i>n</i> -propylcarbinol	1.1103	20	-0.23	-0.26	-0.40	-2.07	-2.34	-3.60	-2.98	-3.37	-5.19	
<i>d</i> -Ethyl- <i>n</i> -butylcarbinol	1.0834	"	-1.62	-1.96	-3.68	-14.96	-18.10	-33.06	-23.83	-28.61	-52.24	
<i>d</i> -Ethyl- <i>n</i> -amylcarbinol	1.1128	"	-1.70	-2.04	-3.75	-15.27	-18.32	-33.69	-26.26	-31.82	-57.94	
<i>d</i> -Ethyl- <i>n</i> -hexylcarbinol	1.0228	"	-1.83	-2.18	-3.95	-17.89	-21.31	-38.62	-33.29	-39.65	-71.83	
<i>l</i> -Ethyl- <i>n</i> -heptylcarbinol	1.0078	"	+1.54	+1.83	+3.47	+15.28	+18.16	+34.43	+30.56	+36.32	+68.86	
<i>l</i> -Ethyl- <i>n</i> -octylcarbinol	1.0390	"	1.48	1.78	3.39	14.24	17.13	32.63	30.49	36.66	69.82	
<i>l</i> -Ethyl- <i>n</i> -nonylcarbinol	1.0771	"	1.29	1.52	2.88	13.10	15.44	29.25	29.86	35.19	66.68	
<i>l</i> -Ethyl- <i>n</i> -decylcarbinol	1.0947	"	1.62	1.82	3.36	14.12	16.90	31.12	34.7	40.90	75.50	
<i>l</i> -Ethyl- <i>n</i> -undecylcarbinol	1.1276	"	1.57	1.90	3.50	13.92	16.85	31.03	35.63	43.13	79.45	
<i>l</i> -Ethyl- <i>n</i> -dodecylcarbinol	1.0981	"	1.47	1.76	3.28	13.38	16.01	29.84	36.11	42.23	80.68	
<i>l</i> -Ethyl- <i>n</i> -tridecylcarbinol	1.1382	"	1.41	1.73	3.23	12.39	15.20	28.39	35.19	43.17	80.61	
<i>l</i> -Ethyl- <i>n</i> -pentadecylcarbinol	1.2214	"	1.41	1.66	3.08	11.54	13.59	25.23	36.03	42.42	75.72	

TABLE XV.

Determinations of Rotatory Powers of the n-Heptates of the Carbinols, C₂H₅CH(OH)·R, in (approx.) 5 per cent. Ethyl-alcoholic Solution.

	Weight of solute. Grams.	Length of tube. cm.	α_D^{20}	α_D^{25}	α_D^{30}	$[\alpha]_D^{20}$	$[\alpha]_D^{25}$	$[\alpha]_D^{30}$	$[M]_D^{25}$	$[M]_D^{30}$	$[M]_D^{35}$
<i>n</i> -Heptate of <i>d</i> - β -Butanol	1.0261	20	+1.85°	+2.17°	+3.59°	+18.03°	+21.16°	+34.96°	+33.55°	+39.34°	+65.08°
Diethylcarbinol	Inactive.								
<i>γ</i> -Hexanol	1.1451	22	+0.01	+0.02	+0.04	+0.03	+0.16	+0.32	+0.17	+0.34	+0.68
<i>d</i> - γ -Heptanol	1.1108	"	-0.39	-0.42	-0.79	-3.19	-3.44	-6.46	-7.28	-7.83	-14.73
<i>d</i> - γ -Octanol	1.1119	20	-0.30	-0.35	-0.65	-2.70	-3.15	-5.84	-6.53	-7.82	-14.15
<i>d</i> - γ -Nonanol	1.0341	22	-0.39	-0.46	-0.81	-3.67	-4.32	-7.61	-9.39	-11.04	-19.49
<i>d</i> - γ -Tridecanol	0.9098	"	-0.34	-0.27	-0.51	-2.40	-2.70	-5.09	-7.48	-8.42	-15.90
<i>l</i> - γ -Tetradecanol	1.1127	"	+0.30	-0.36	-0.73	+2.45	-2.94	-5.96	+7.99	-9.58	-19.44
<i>l</i> - γ -Pentadecanol	0.8795	"	+0.26	+0.33	+0.60	+2.99	+3.41	+6.20	+9.14	+11.61	+21.10
<i>l</i> - γ -Hexadecanol	1.2542	"	+0.29	+0.35	+0.76	+3.40	+2.54	+5.61	+7.44	+8.98	+19.50
<i>l</i> - γ -Octadecanol	1.2203	"	+0.26	+0.31	+0.62	+1.94	+2.31	+4.62	+7.40	+8.82	+17.64

TABLE XVI.
Determinations of Rotatory Powers of the n-Heptoates of the Carbinols, C₂H₅CH(OH)·R, in 5 per cent. Carbon Disulphide Solution.

	Weight of solute.	Length of tube.	α_D	α_{470}	α_{410}	$[\alpha]_D^{25}$	$[\alpha]_{470}^{25}$	$[\alpha]_{410}^{25}$	$[M]_D^{25}$	$[M]_{470}^{25}$	$[M]_{410}^{25}$
n-Heptoate of	Grams.	cm.									
d- β -Butanol	1.2376	20	+1.01°	+1.18°	+1.79°	+8.16°	+9.53°	+14.46°	+15.17°	+17.73°	+26.80°
l- γ -Hexanol	1.0639	"	+0.22	+0.36	+0.65	+2.07	+2.04	+5.17	+4.42	+5.23	+11.10
d- γ -Heptanol	1.1943	"	-1.27	-1.63	-2.85	-10.64	-12.98	-23.86	-24.25	-23.69	-54.42
d- γ -Octanol	1.1405	"	-1.23	-1.25	-2.79	-10.79	-13.33	-24.47	-26.11	-32.26	-59.23
d- γ -Nonanol	1.0007	"	-1.34	-1.61	-2.83	-13.40	-16.10	-28.30	-34.30	-41.21	-72.44
d- γ -Tridecanol	1.0481	"	-1.10	-1.32	-2.40	-10.50	-12.60	-22.90	-32.75	-39.30	-71.45
l- γ -Tetradecanol	1.1392	"	+1.24	+1.51	+2.82	+10.88	+13.25	+24.75	+35.48	+43.21	+80.69
l- γ -Pentadecanol	1.0672	"	+1.14	+1.40	+2.50	+10.69	+13.12	+23.81	+36.34	+44.62	+80.95
l- γ -Hexadecanol	1.0773	"	+1.10	+1.29	+2.45	+10.21	+11.98	+22.75	+36.16	+42.40	+80.54
l- γ -Octadecanol	1.2533	"	+1.06	+1.27	+2.40	+8.46	+10.14	+19.15	+32.31	+38.72	+73.16

*Density Determinations.**Esters of d-γ-Nonanol.*

Acetate :						
<i>t</i>	12°	31°	45°	67.5°	86°	123.5°
<i>D</i> ₄ ⁱ	0.8685	0.8526	0.8402	0.8212	0.8051	0.7708
Propionate :						
<i>t</i>	12°	43°	69°	95°		
<i>D</i> ₄ ⁱ	0.8660	0.8420	0.8195	0.7962		
<i>n</i> -Butyrate :						
<i>t</i>	17°	53°	86°	132°		
<i>D</i> ₄ ⁱ	0.8602	0.8310	0.8027	0.7619		
<i>n</i> -Valerate :						
<i>t</i>	16.5°	58°	95°	134°		
<i>D</i> ₄ ⁱ	0.8587	0.8269	0.7957	0.7630		
<i>n</i> -Hexoate :						
<i>t</i>	15°	55°	85°	123°		
<i>D</i> ₄ ⁱ	0.8593	0.8295	0.8052	0.7742		
<i>n</i> -Heptoate :						
<i>t</i>	16.5°	52.5°	86°	126.5°		
<i>D</i> ₄ ⁱ	0.8600	0.8320	0.8052	0.7714		
<i>n</i> -Octoate :						
<i>t</i>	17°	57°	90.5°	134°		
<i>D</i> ₄ ⁱ	0.8583	0.8287	0.8021	0.7670		
<i>n</i> -Nonoate :						
<i>t</i>	16°	56°	93°	131°		
<i>D</i> ₄ ⁱ	0.8586	0.8301	0.8020	0.7735		
<i>n</i> -Decoate :						
<i>t</i>	17°	54°	86°	128°		
<i>D</i> ₄ ⁱ	0.8576	0.8305	0.8071	0.7744		
<i>n</i> -Undecoate :						
<i>t</i>	14°	54°	93°	134.6°		
<i>D</i> ₄ ⁱ	0.8588	0.8301	0.8000	0.7694		
<i>n</i> -Dodecoate :						
<i>t</i>	16°	56.5°	99.5°	134°		
<i>D</i> ₄ ⁱ	0.8600	0.8312	0.7990	0.7757		
Myristate :						
<i>t</i>	18.5°	50.5°	91°	126.5°		
<i>D</i> ₄ ⁱ	0.8567	0.8351	0.8055	0.7791		
Palmitate :						
<i>t</i>	17°	60°	93.5°	130.5°		
<i>D</i> ₄ ⁱ	0.8575	0.8272	0.8035	0.7774		
Stearate :						
<i>t</i>	24°	57°	96.5°	139°		
<i>D</i> ₄ ⁱ	0.8543	0.8303	0.8027	0.7735		

Density Determinations (continued).

 Acetates of
d- γ -Hexanol :

<i>t</i>	20°	52.5°	87°	115°
D _d ^t	0.8672	0.8376	0.8007	0.7731

d- γ -Heptanol :

<i>t</i>	20°	56°	84°	129.5°
D _d ^t	0.8647	0.8317	0.8051	0.7593

d- γ -Octanol :

<i>t</i>	15°	53°	85°	115°
D _d ^t	0.8705	0.8388	0.8073	0.7771

l- γ -Decanol :

<i>t</i>	18.5°	52°	86°	126°
D _d ^t	0.8662	0.8376	0.8078	0.7697

l- γ -Undecanol :

<i>t</i>	17°	56°	90°	134°
D _d ^t	0.8652	0.8355	0.8042	0.7654

l- γ -Dodecanol :

<i>t</i>	16°	54.5°	92°	129°
D _d ^t	0.8627	0.8350	0.8038	0.7717

l- γ -Tridecanol :

<i>t</i>	14°	54°	92.5°	135.5°
D _d ^t	0.8653	0.8368	0.8054	0.7669

l- γ -Tetradecanol :

<i>t</i>	16°	56°	99.5°	122°
D _d ^t	0.8638	0.8341	0.7996	0.7839

l- γ -Pentadecanol :

<i>t</i>	18.5°	50°	91°	126.5°
D _d ^t	0.8611	0.8381	0.8072	0.7804

l- γ -Hexadecanol :

<i>t</i>	17°	60°	93°	130.5°
D _d ^t	0.8613	0.8313	0.8052	0.7754

l- γ -Octadecanol :

<i>t</i>	24°	57°	97.5°	137°
D _d ^t	0.8571	0.8341	0.8049	0.7752

*Observed Rotations ($\alpha_{100\text{ mm.}}$) in the Homogeneous State of the
Esters of d- γ -Nonanol.*

Acetate :

t	19°	51°	70°	89°	133°	160°
α_D	-4.50°	-4.38°	-4.30°	-4.26°	-4.18°	-4.08°
t	19°	50°	70°	104°	133°	160°
α_{gr}	-5.40°	-5.30°	-5.18°	-5.14°	-5.06°	-4.92°
t	19°	50°	70°	106°	133°	164°
α_{vi}	-9.90°	-9.58°	-9.40°	-9.30°	-9.02°	-8.82°

Propionate :

t	21°	70°	100°	126°	155°	
α_D	-5.02°	-4.43°	-4.26°	-4.12°	-3.94°	
t	21°	63°	100°	126°	155°	
α_{gr}	-6.00°	-4.50°	-5.20°	-4.92°	-4.80°	
t	21°	63°	100°	126°	157°	
α_{vi}	-10.76°	-9.88°	-9.28°	-8.86°	-8.42°	

n-Butyrate :

t	20°	72°	117°	175°		
α_D	-2.92°	-2.60°	-2.42°	-2.22°		
t	20°	72°	118°	174°		
α_{gr}	-3.52°	-3.26°	-3.02°	-2.70°		
t	20°	72°	118°	174°		
α_{vi}	-6.52°	-6.00°	-5.60°	-5.20°		

n-Valerate :

t	19°	70°	121°	168°		
α_D	-2.63°	-2.30°	-2.02°	-1.84°		
t	19°	68°	121°	149°	168°	
α_{gr}	-3.30°	-3.00°	-2.54°	-2.38°	-2.24°	
t	19°	68°	121°	149°	168°	
α_{vi}	-6.16°	-5.46°	-4.80°	-4.40°	-4.20°	

n-Hexoate :

t	17°	60°	128°	186°		
α_D	-2.32°	-2.00°	-1.66°	-1.40°		
t	17°	62°	128°	186°		
α_{gr}	-2.86°	-2.54°	-2.10°	-1.76°		
t	17°	62°	126°	186°		
α_{vi}	-5.38°	-4.76°	-4.02°	-3.38°		

n-Heptoate :

t	19°	52°	89°	169°		
α_D	-2.02°	-1.84°	-1.64°	-1.26°		
t	19°	53°	89°	168°		
α_{gr}	-2.52°	-2.26°	-2.04°	-1.68°		
t	19°	53°	91°	168°		
α_{vi}	-4.82°	-4.32°	-3.78°	-3.12°		

n-Octoate :

t	22°	65°	110°	169°		
α_D	-1.80°	-1.56°	-1.34°	-1.04°		
t	24°	70°	110°	169°		
α_{gr}	-2.16°	-1.96°	-1.76°	-1.48°		
t	24°	70°	110°	169°		
α_{vi}	-4.18°	-3.86°	-3.42°	-2.76°		

*Observed Rotations ($\alpha_{100 \text{ mm}}$) in the Homogeneous State of the
Esters of γ -Nonanol (continued).*

n-Nonoate :

<i>t</i>	22°	73°	115°	171°
α_D	-1.66°	-1.42°	-1.24°	-0.94°
<i>t</i>	22°	67°	114°	168°
α_{gr}	-2.10°	-1.84°	-1.60°	-1.36°
<i>t</i>	22°	69°	114°	
α_{vi}	-3.90°	-3.52°	-3.12°	

n-Decoate :

<i>t</i>	19°	60°	113°	147°	170°
α_D	-1.64°	-1.42°	-1.24°	-1.10°	-1.02°
<i>t</i>	19°	64°	112°	171°	
α_{gr}	-2.10°	-1.90°	-1.64°	-1.34°	
<i>t</i>	19°	75°	112°	171°	
α_{vi}	-3.76°	-3.26°	-3.10°	-2.60°	

n-Undecoate :

<i>t</i>	20°	69°	127°	160°
α_D	-1.56°	-1.48°	-1.14°	-0.98°
<i>t</i>	20°	67°	127°	160°
α_{gr}	-1.94°	-1.82°	-1.40°	-1.24°
<i>t</i>	20°	67°	124°	162°
α_{vi}	-3.70°	-3.36°	-2.62°	-2.32°

n-Dodecoate :

<i>t</i>	19°	62°	117°	154°
α_D	-1.40°	-1.20°	-1.00°	-0.84°
<i>t</i>	19°	60°	117°	154°
α_{gr}	-1.78°	-1.52°	-1.30°	-1.16°
<i>t</i>	19°	60°	117°	154°
α_{vi}	-3.32°	-2.90°	-2.42°	-2.18°

Myristate :

<i>t</i>	18°	63°	80°	104°	145°	168°
α_D	-1.34°	-1.20°	-1.16°	-1.00°	-0.96°	-0.82°
<i>t</i>	18°	80°	103°	120°	145°	168°
α_{gr}	-1.72°	-1.44°	-1.36°	-1.30°	-1.20°	-1.06°
<i>t</i>	18°	80°	103°	121°	168°	
α_{vi}	-3.20°	-2.72°	-2.52°	-2.40°	-1.90°	

Palmitate :

<i>t</i>	17°	66°	107°	150°
α_D	-1.30°	-1.14°	-1.04°	-0.88°
<i>t</i>	17°	68°	100°	150°
α_{gr}	-1.60°	-1.38°	-1.28°	-1.08°
<i>t</i>	17°	68°	100°	150°
α_{vi}	-2.88°	-2.56°	-2.40°	-2.10°

Stearate :

<i>t</i>	22°	66°	130°	173°
α_D	-1.26°	-1.18°	-0.94°	-0.86°
<i>t</i>	22°	66°	131°	175°
α_{gr}	-1.52°	-1.42°	-1.14°	-1.08°
<i>t</i>	22°	66°	131°	175°
α_{vi}	-2.70°	-2.50°	-2.00°	-1.86°

n-Nonoate of 1-γ-Nonanol.

t	a_D	a_{gr}	a_{vi}
21°	+1.64°	+2.12°	+4.08°

Acetate of 1-γ-Tetradecanol.

t	18°	61°	105°	151°
a_D	+3.18°	+3.08°	+3.04°	+2.92°
t	18°	60°	105°	152°
a_{gr}	+3.32°	+3.70°	+3.64°	+3.52°
t	18°	60°	105°	152°
a_{vi}	+7.04°	+6.86°	+6.70°	+6.48°

Acetate of 1-γ-Pentadecanol.

t	21°	74°	113°	155°
a_D	+3.16°	+3.04°	+2.92°	+2.82°
t	21°	80°	113°	153°
a_{gr}	+3.80°	+3.64°	+3.54°	+3.44°
t	21°	80°	110°	153°
a_{vi}	+6.96°	+6.64°	+6.50°	+6.32°

Acetate of 1-γ-Hexadecanol.

t	19°	65°	95°	123°	163°
a_D	+2.74°	+2.68°	+2.62°	+2.60°	+2.56°
t	19°	67°	120°		163°
a_{gr}	+3.32°	+3.20°	+3.10°		+3.00°
t	19°	68°	120°		163°
a_{vi}	+6.24°	+5.94°	+5.76°		+5.68°

Acetate of 1-γ-Octadecanol.

t	57°	103°	153°	187°
a_D	+2.52°	+2.40°	+2.38°	+2.30°
t	54°	103°	153°	187°
a_{gr}	+2.96°	+2.86°	+2.76°	+2.64°
t	52°	103°	153°	187°
a_{vi}	+5.60°	+5.40°	+5.28°	+5.08°

Acetate of 1-γ-Decanol.

t	21°	44°	92°	116°	163°
a_D	+3.88°	+3.82°	+3.72°	+3.64°	+3.58°
t	21°	45°	92°	116°	163°
a_{gr}	+4.68°	+4.60°	+4.44°	+4.34°	+4.22°
t	21°	45°	92°	116°	163°
a_{vi}	+8.50°	+8.38°	+8.04°	+7.94°	+7.68°

Acetate of 1-γ-Undecanol.

t	19.5°	72°	110°	161°
a_D	+3.80°	+3.56°	+3.52°	+3.40°
t	19.5°	70°	115°	161°
a_{gr}	+4.38°	+4.26°	+4.18°	+3.94°
t	19.5°	66°	115°	161°
a_{vi}	+8.10°	+7.78°	+7.60°	+7.24°

Acetate of l-γ-Dodecanol.

<i>t</i>	17°	68°	100°	119°	151°
<i>a_D</i>	+3.18°	+2.96°	+2.84°	+2.80°	+2.78°
<i>t</i>	17°	76°	112°	152°	
<i>a_{gr}</i>	+3.82°	+3.54°	+3.30°	+3.24°	
<i>t</i>	17°	74°	112°	153°	
<i>a_{vi}</i>	+7.04°	+6.50°	+6.16°	+6.06°	

Acetate of l-γ-Tridecanol.

<i>t</i>	17°	87°	110°	171°	
<i>a_D</i>	+3.30°	+3.18°	+3.14°	+2.98°	
<i>t</i>	17°	85°	110°	171°	
<i>a_{gr}</i>	+3.98°	+3.84°	+3.76°	+3.54°	
<i>t</i>	17°	85°	110°	171°	
<i>a_{vi}</i>	+7.34°	+6.90°	+6.82°	+6.58°	

Acetate of d-γ-Hexanol.

<i>t</i>	20°	73°	115°	127°	
<i>a_D</i>	+0.48°	+0.44°	+0.38°	+0.34°	
<i>t</i>	20°	72°	107°	129°	
<i>a_{gr}</i>	+0.56°	+0.52°	+0.46°	+0.38°	
<i>t</i>	20°	69°	109°	130°	
<i>a_{vi}</i>	+0.62°	+0.56°	+0.50°	+0.46°	

Acetate of d-γ-Heptanol.

<i>t</i>	20°	73°	105°	131°	
<i>a_D</i>	-4.06°	-3.88°	-3.82°	-3.80°	
<i>t</i>	20°	71°	105°	130°	
<i>a_{gr}</i>	-4.90°	-4.76°	-4.63°	-4.60°	
<i>t</i>	20°	71°	105°	130°	
<i>a_{vi}</i>	-9.02°	-8.76°	-8.54°	-8.32°	

Acetate of d-γ-Octanol.

<i>t</i>	24°	72°	126°	157°	
<i>a_D</i>	-3.74°	-3.66°	-3.62°	-3.58°	
<i>t</i>	24°	68°	127°	157°	
<i>a_{gr}</i>	-4.40°	-4.32°	-4.28°	-4.22°	
<i>t</i>	24°	68°	129°	159°	
<i>a_{vi}</i>	-8.34°	-8.16°	-7.98°	-7.70°	

The author has much pleasure in acknowledging his indebtedness to the Government Grant Committee of the Royal Society for a Grant which has defrayed some of the expenses of this investigation.

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CCX.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part VIII. The Optical Rotatory Powers of the Normal Esters of Methylbenzylcarbinol.*

By JOSEPH KENYON and ROBERT HOWSON PICKARD.

It has been shown recently (compare Parts V. and VI., this vol., pp. 830 and 1115) that some optically active esters of the simplest possible chemical constitution exhibit, both in the homogeneous state at temperatures above the normal and in certain solvents, the phenomenon commonly known as anomalous rotatory dispersion. Further, such esters, at least under those conditions, do not conform to the law of simple optical rotatory dispersion represented by the equation $\alpha = k/\lambda^2 - \lambda_0^2$, which was first suggested by Drude, and lately (T., 1913, 103, 1067) confirmed by Lowry. These esters were prepared from normal fatty acids and the optically active carbinols of the formula $\text{CH}_3\text{CH}(\text{OH})\cdot\text{R}$ (where R=a normal alkyl group) (see Part I., T., 1911, 99, 45). The rotatory powers of the carbinols themselves have been shown (Lowry, Pickard and Kenyon, this vol., p. 94) to conform to the law of simple optical rotatory dispersion, whilst the dispersions have been found to be constant over a wide range of temperature (see Part IV., T., 1913, 103, 1931), so that the anomalous dispersion of the esters can be ascribed most probably to some property of the carboxylic group.

The great mass of material used in previous investigations on rotatory power is composed mainly of esters, and the rotatory powers of few of these have been determined over a wide range of temperature or for light of more than one wave-length. Therefore it appeared of immediate interest to investigate other homologous series of esters prepared from carbinols of simple chemical constitution and containing more complex radicles than normal alkyl groups. For this purpose, *d*-methylbenzylcarbinol (Part VI., *loc. cit.*) is admirably suited; it has a fairly high rotatory power which, like its dispersive power, is only slightly affected by variations of temperature, whilst the determinations of its rotatory power (this vol., p. 1122) appear at all temperatures to conform strictly to the law of simple optical rotatory dispersion.* In the experimental part of this paper, the preparation of fourteen esters of *d*-methylbenzylcarbinol with normal fatty acids is described, and

* Since the reciprocals of the observed rotations, when plotted against the squares of wave-lengths, fall on a straight line.

they have been investigated in much the same manner as was adopted for the other eight homologous series of esters previously described (Part V., *loc. cit.*).

The optical properties of this homologous series (from the acetate to the stearate of the carbinol) are analogous to those of the other series of esters. Thus the molecular rotatory powers of the esters in the homogeneous state continually increase in magnitude as the series is ascended, the increment being large until the *n*-valerate is reached, and afterwards much smaller. This phenomenon (see table I) is to be observed at all temperatures when the esters are examined in the homogeneous state, and also in 5 per cent. solution in ethyl alcohol and in carbon disulphide,* although under some conditions the acetate is somewhat abnormal. The values of the molecular rotatory powers when plotted (see Fig. 1) show that the

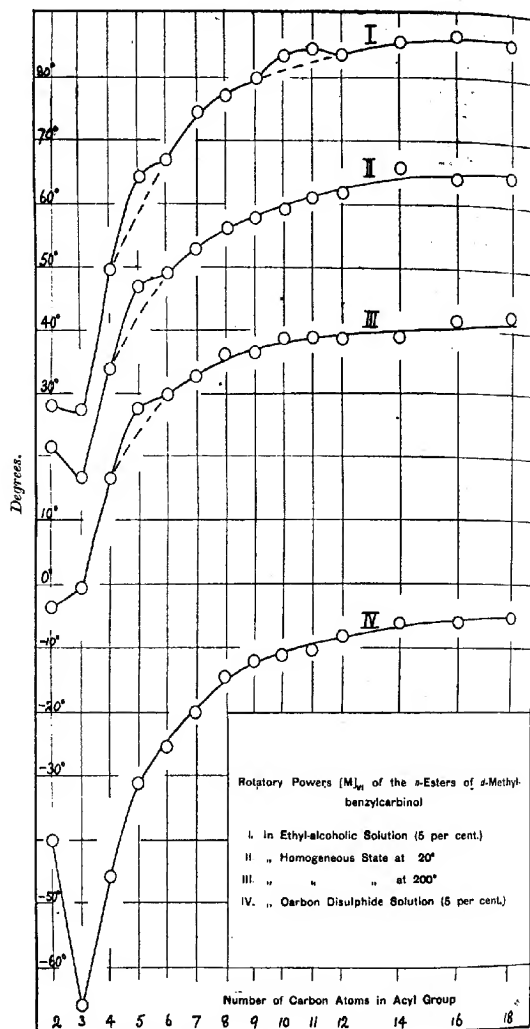
TABLE I.
*Molecular Rotatory Powers, $[M]_{D^{25}}$, of the Esters of
d-Methylbenzylcarbinol.*

	Homogeneous state		5 per cent. solution	
	at 20°.	at 200°.	in ethyl alcohol.	in carbon disulphide.
Acetate	+21.56°	-3.87°	+27.99°	-40.15°
Propionate	16.67	-0.92	27.10	-66.37
<i>n</i> -Butyrate	33.81	+16.45	49.45	-45.93
<i>n</i> -Valerate	46.62	27.36	64.31	-31.26
<i>n</i> -Hexoate	48.95	29.61	66.85	-25.64
<i>n</i> -Hexoate	52.73	32.58	74.37	-20.13
<i>n</i> -Heptoate	56.11	36.23	76.81	-14.59
<i>n</i> -Octoate	57.71	36.17	79.64	-12.29
<i>n</i> -Nonoate	58.88	38.94	83.30	-11.37
<i>n</i> -Decoate	60.82	38.81	84.26	-10.68
<i>n</i> -Dodecoate	61.67	38.57	83.41	-8.58
Myristate	66.61	38.87	85.65	-6.29
Palmitate	63.97	41.50	86.88	-6.39
Stearate	64.25	42.85	85.21	-5.25

general relation of the values as determined under the four different conditions is similar, whilst it will be seen that the values (with the remarkable exception of those obtained in carbon disulphide solution) of the molecular rotatory power of the *n*-valerate show an additional exaltation over what may be called the normal rate of increment as deduced from the shape of the curves. The latter phenomenon, whilst it has not hitherto been observed for esters of secondary alcohols containing a methyl group (compare, however, Part VII., this vol., p. 2230), is an outstanding feature of

* Slight deviations from this statement in a few instances are to be ascribed to the magnification of the experimental errors in the calculation of the molecular rotatory power.

FIG. 1.



the homologous series of carbinols recently described (*loc. cit.*), and is, of course, to be ascribed to the special configuration of the valerate in which the growing chain $\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3$ may be assumed from stereochemical considerations to all but return on itself. There are indications that this phenomenon recurs in the series at the decoate and undecoate when the growing chain may be assumed again to return on itself, but as the molecular weight of these esters is large there is some uncertainty about the correctness of the values given for the molecular rotatory powers. It will be seen that the general behaviour of these esters is somewhat similar to that of those derived from the simpler carbinols; thus increase of temperature, and particularly solution in carbon disulphide, depress the rotatory power of the esters as determined in the homogeneous state at 20° , but solution in ethyl alcohol slightly increases the same.

Temperature has a common effect on all the members of the series, and the values of the rotatory powers (see pp. 2271—2273) when plotted (Fig. 2) form a series of "temperature-rotation" curves which are very similar, and gradually diminish in slope (that is, in the temperature-coefficient) as the molecular weight increases. When the temperature is sufficiently high to depress the specific rotatory power, $[\alpha]_D$, to about $+1^\circ$, the phenomenon of anomalous rotatory dispersion (as regards light of wave-length extending from that for yellow sodium light to violet mercury light) can be observed. Actually, however, this has been done only for the acetate (see Fig. 3*) and propionate, as the experimental conditions did not permit of readings at (or extrapolation to) above 200° . The slope of the temperature-rotation curves, however, justifies the above-stated generalisation, and it is further obvious that concentrated solutions of any of the esters in carbon disulphide will show anomalous rotatory dispersion. This phenomenon will of necessity be exhibited by all substances the rotations of which change sign under any given condition, such as temperature or solution, except for those substances the rotatory powers of which pass through zero under the same conditions for light of all wave-lengths.

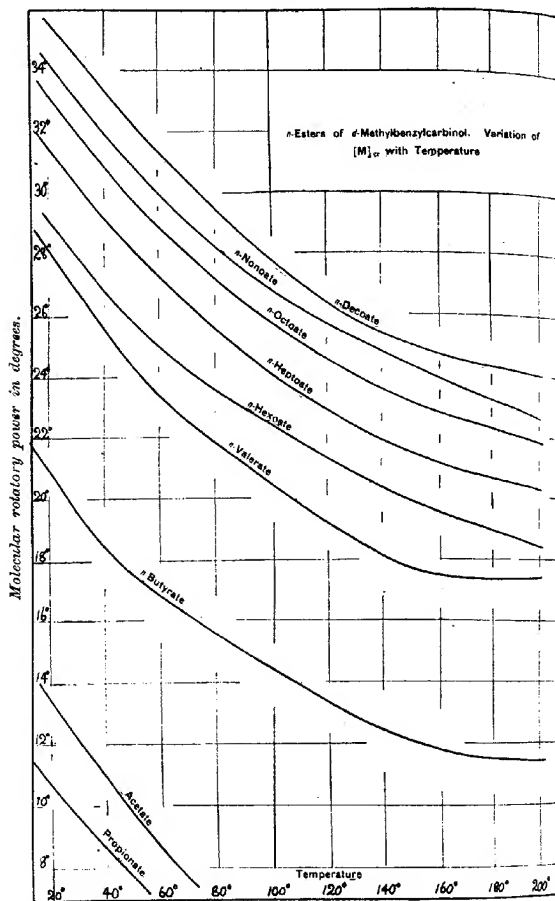
The anomalous† rotatory dispersion of the esters now described can be best explained by assuming the presence in the apparently homogeneous esters of two isomerides, varying in optical sign and dispersive power, and of the type suggested in Part V. It is com-

* The curves do not intersect all in one point.

† It may quite easily be that this behaviour may be not abnormal as regards the optically active substances now known, but may be the more common particularly as most of these are esters.

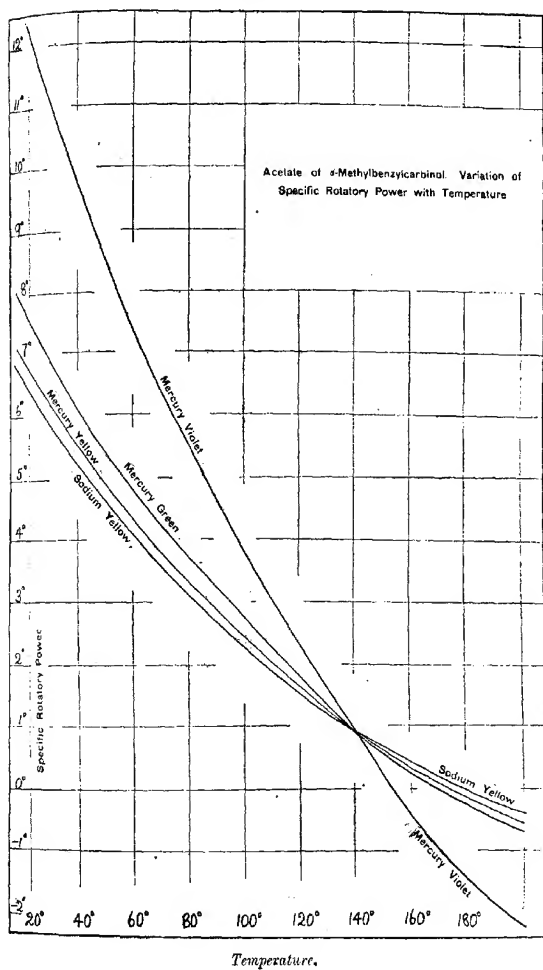
paratively easy to imagine the interconversion of such isomerides under the experimental conditions, but not so easy to account for

FIG. 2.



the necessarily great difference in the optical properties of each. Until further evidence of this kind is accumulated, it is worth while to note that in support of this assumption of an elusive form

FIG. 3.



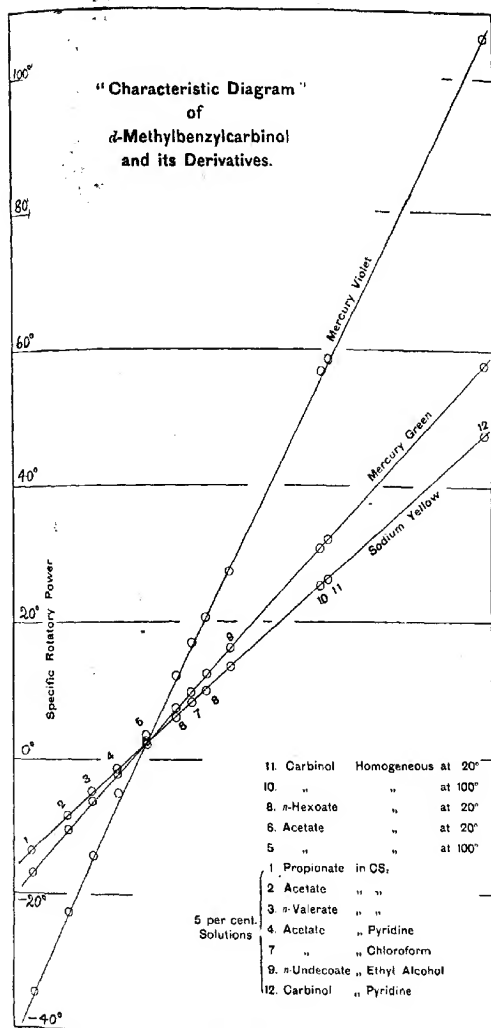
of isomerism ("elusive" in the sense that the isomerides cannot be separated, are very labile, and owe their existence probably to what have been called "latent" valencies), the small differences in structure due to *cis*- and *trans*-isomerism are sufficient to cause great difference in optical properties; thus in each of the two stereochemical pairs of compounds *L*-borneol and *d*-isoborneol, which correspond with *L*-camphor, and *L*-menthol and *d*-neomenthol, which correspond with *L*-menthone (Pickard and Littlebury, T., 1907, 91, 1974; T., 1912, 101, 109), the two modifications have rotatory powers of opposite sign and of different magnitude and different dispersive powers.

The deduction from such an assumption, made in the form of a "characteristic diagram" for substances showing anomalous rotatory dispersive power by Armstrong and Walker (*Proc. Roy. Soc.*, 1913, [A], 88, 388), and extended by the present authors (Part V, *loc. cit.*) to correlate the values of the rotatory powers of a series of (analogous or) homologous compounds, is well illustrated in the characteristic diagram (Fig. 4) for methylbenzylcarbinol and its esters. This method of plotting is fully described in Part V, and it is most striking that it allows of the correlation of values of the specific rotatory powers of this carbinol and its esters over a range from $+169^\circ$ to -34° .

In respect to the dispersive power, these esters of methylbenzylcarbinol are quite analogous to those of the "methyl" series of carbinols, $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{R}$. Thus at the ordinary temperature they appear to conform strictly to the law of simple dispersive power $\alpha = k/\lambda^2 - \lambda_0^2$, but with increase of temperature the dispersive power becomes more complex. It therefore appears that the esters may be *really* homogeneous at the lower temperatures, and become mixtures of labile isomerides on increase of temperature. Such results, along with deductions drawn from the similarity of the temperature-rotation curves (compare Part I, *loc. cit.*, p. 53), appear to be against the possible assumption of a polymeric form of association to account for the variations in the rotatory powers of these esters. It is easy to formulate, for example, a bimolecular form of an ester, but there are many physical data relating to esters of all kinds which seem to point to an absence of polymerism in the esters of simple chemical constitution.

The determinations of the rotatory power in different solvents of *d*- β -octanol, its acetate, heptoate and stearate, of *d*- β -butanol and its acetate (this vol., p. 881 *et seq.*), and of *d*-methylbenzylcarbinol (*ibid.*, p. 1129) and its acetate (p. 2274), seem to show that (1) solvents have (generally speaking) a common effect on the rotatory powers of compounds of similar constitution, and

FIG. 4.



(2) the sequence in magnitude of the rotatory powers exhibited by a compound in different solvents does not depend on any one physical property of the solvents. The effect of solution in carbon disulphide (and to a less degree in pyridine) of all the esters described in this series of investigations is to depress the rotatory power exhibited in the homogeneous state, and in the majority of cases this depression is accompanied by a change of sign.

EXPERIMENTAL.

The *d*-methylbenzylcarbinol was prepared in quantities of 100 c.c. by the method described in Part VI. The acetate, propionate, and butyrate were obtained by treating the carbinol with the respective anhydrides, and the remaining esters by the treatment of the carbinol dissolved in pyridine with the required acid chloride. The esters (see table II) were obtained as clear, colourless liquids, of which the palmitate and stearate solidified in the ice-box to crystalline masses, melting respectively at 20.5° and 28.5°. All residues from the preparation and distillation of the esters were collected and hydrolysed; the carbinol thus obtained, as well as that from the hydrolysis of a mixture prepared at the end of the experimental work from all the pure esters, was unaltered in rotatory power. The esters have only faint odours.

The procedure in the determinations of rotatory power and density was the same as described in Part VI. (*loc. cit.*), except that the rotatory power was also determined for the yellow mercury light as well as for the green and violet.

TABLE II.

Esters of d-Methylbenzylcarbinol.

	B. p.	D ₂₀ [°] .	n _D ²⁰ .	n - 1/d. M.
Acetate	115°/16 mm.	0.9991	1.4897	87.2
Propionate ...	121°/15 "	0.9890	1.4863	94.4
n-Butyrate	132°/16 "	0.9749	1.4825	102.0
n-Valerate ...	148°/16 "	0.9648	1.4812	109.7
n-Hexoate	161°/14 "	0.9560	1.4806	117.6
n-Heptoate	135°/4 "	0.9479	1.4797	125.5
n-Octoate	144°/3 "	0.9420	1.4793	133.2
n-Nonoate	151°/4 "	0.9377	1.4784	140.8
n-Decoate	163°/4 "	0.9310	1.4775	148.8
n-Undecoate ...	170°/4 "	0.9270	1.4774	156.6
n-Dodecoate ...	183°/5 "	0.9230	1.4772	164.4
Myristate	192°/2 "	0.9196	1.4764	179.3
Palmitate	235°/8 "	0.9130	1.4760	195.0
Stearate	215°/2 "	0.9120	—	—

TABLE III.

*Rotations of the Esters at Different Temperatures.**d*-MethylbenzylcarbinyI Acetate, $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_3$.

Temp.	D_1°	$[\alpha]_D$	$[\alpha]_{57}$	$[\alpha]_{57}$	$[\alpha]_{57}$	$[\alpha]_{57}$	$[\alpha]_{57}$	$[\alpha]_{57}$	$[\alpha]_{57}$
20°	0.9991	+6.41°	+6.71°	+7.54°	+12.12°	+11.40°	+11.93°	+13.42°	+21.58°
40	0.9860	5.27	5.49	6.11	9.64	9.39	9.77	10.88	17.17
60	0.9699	4.10	4.30	4.78	7.32	7.30	7.65	8.51	13.03
80	0.9510	3.05	3.27	3.71	5.45	5.43	5.82	6.81	9.60
100	0.9310	2.31	2.44	2.76	3.78	4.11	4.34	4.91	6.73
120	0.9103	1.66	1.65	1.76	2.18	2.78	2.93	3.13	3.87
140	0.8886	0.92	0.90	0.92	0.87	1.64	1.80	1.64	1.64
160	0.8660	0.38	0.26	0.17	-0.37	0.68	0.47	0.31	-0.66
180	0.8430	-0.06	-0.15	-0.27	-1.47	-0.10	-0.27	-0.48	-2.62
200	0.8180	-0.37	-0.66	-0.67	-2.18	-0.65	-1.00	-1.20	-3.87

d-MethylbenzylcarbinyI Propionate, $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{O}\cdot\text{CO}\cdot\text{C}_2\text{H}_5$.

20°	0.9890	+4.81°	+5.06°	+5.58°	+8.69°	+9.23°	+9.71°	+10.72°	+16.67°
40	0.9711	3.89	4.09	4.47	6.76	7.47	7.85	8.58	12.97
60	0.9537	3.04	3.25	3.50	5.14	5.84	6.24	6.72	9.86
80	0.9354	2.33	2.51	2.67	3.79	4.47	4.82	5.13	7.28
100	0.9165	1.83	1.96	2.13	2.73	3.52	3.77	4.08	5.24
120	0.8973	1.48	1.56	1.65	1.96	2.85	2.99	3.17	3.76
140	0.8778	1.20	1.20	1.20	1.20	2.30	2.30	2.30	2.30
160	0.8578	0.99	0.93	0.87	0.58	1.90	1.79	1.68	1.12
180	0.8380	0.83	0.72	0.66	±0.00	1.60	1.37	1.26	±0.00
200	0.8180	0.73	0.67	0.49	-0.48	1.41	1.29	0.94	-0.92

d-MethylbenzylcarbinyI *n*-Butyrate, $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{O}\cdot\text{CO}\cdot\text{C}_3\text{H}_7$.

20°	0.9749	+8.48°	+8.94°	+10.14°	+16.41°	+17.48°	+18.43°	+20.87°	+33.81°
40	0.9571	7.57	7.95	8.93	14.53	15.61	16.39	18.41	29.94
60	0.9397	6.92	7.24	8.14	13.21	14.25	14.90	16.77	27.23
80	0.9220	6.40	6.70	7.53	12.04	13.18	13.81	15.61	24.80
100	0.9044	6.00	6.30	7.01	11.04	12.37	12.98	14.44	22.73
120	0.8865	5.54	5.80	6.49	10.06	11.41	11.95	13.37	20.71
140	0.8685	5.22	5.41	6.04	9.30	10.74	11.15	12.46	19.16
160	0.8505	4.96	5.14	5.76	8.77	10.22	10.59	11.87	18.07
180	0.8330	4.87	4.96	5.56	8.29	10.04	10.22	11.45	17.09
200	0.8150	4.91	5.03	5.56	7.99	10.10	10.36	11.45	16.45

d-MethylbenzylcarbinyI *n*-Valerate, $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{O}\cdot\text{CO}\cdot\text{C}_4\text{H}_9$.

20°	0.9648	+10.76°	+11.28°	+12.79°	+21.19°	+23.69°	+24.80°	+28.14°	+46.62°
40	0.9476	9.94	10.39	11.69	19.53	21.87	22.84	25.71	42.95
60	0.9306	9.13	9.52	10.68	17.70	20.09	20.94	23.28	38.95
80	0.9134	8.48	8.89	9.84	16.42	18.66	19.55	21.65	36.13
100	0.8962	7.97	8.34	9.28	15.29	17.53	18.34	20.42	33.55
120	0.8790	7.59	7.75	8.75	14.16	16.69	17.04	19.24	31.16
140	0.8617	7.08	7.31	8.21	13.11	15.57	16.08	18.07	28.85
160	0.8442	6.76	6.89	7.90	12.56	14.82	15.17	17.38	27.56
180	0.8270	6.76	6.96	7.86	12.30	14.85	15.32	17.29	27.13
200	0.8098	6.82	7.04	7.90	12.44	14.99	15.48	17.39	27.36

TABLE III. (continued).

d-Methylbenzylcarbinyl n-Hexoate, $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_{11}$.										
Temp.	D_4°	$[\alpha]_D$	$[\alpha]_{25}$	$[\alpha]_{35}$	$[\alpha]_{45}$	$[\text{M}]_D$	$[\text{M}]_{25}$	$[\text{M}]_{35}$	$[\text{M}]_{45}$	
20°	0.9560	+10.46°	+11.21°	+12.46°	+20.91°	+24.47°	+26.25°	+29.15°	+48.95°	
40	0.9394	9.58	10.20	11.41	18.84	22.42	23.92	26.70	44.09	
60	0.9230	8.88	9.45	10.62	17.34	20.79	22.11	24.84	40.56	
80	0.9064	8.46	8.82	10.01	16.31	19.80	20.64	23.42	38.18	
100	0.8898	8.09	8.43	9.55	15.54	18.93	19.72	22.36	36.33	
120	0.8731	7.77	8.13	9.16	14.89	18.18	19.03	21.44	34.64	
140	0.8563	7.47	7.79	8.76	14.19	17.49	18.23	20.49	33.20	
160	0.8394	7.18	7.50	8.31	13.55	16.81	17.56	19.45	31.70	
180	0.8228	7.05	7.29	8.02	13.06	16.49	17.06	18.77	30.57	
200	0.8061	6.95	7.19	7.88	12.66	16.26	16.84	18.45	29.61	
d-Methylbenzylcarbinyl n-Heptoate, $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_{13}$.										
20°	0.9479	+10.69°	+11.34°	+12.72°	+21.26°	+26.51°	+28.13°	+31.54°	+52.73°	
40	0.9320	9.98	10.45	11.80	19.53	24.75	25.93	29.25	48.44	
60	0.9163	9.33	9.76	11.03	18.28	23.15	24.19	27.34	45.34	
80	0.9002	8.86	9.21	10.32	17.00	21.99	22.84	25.60	42.16	
100	0.8805	8.39	8.69	9.69	15.90	20.82	21.55	24.03	39.44	
120	0.8666	8.00	8.29	9.19	15.11	19.85	20.56	22.79	37.49	
140	0.8528	7.62	7.92	8.82	14.60	18.91	19.63	21.87	36.21	
160	0.8370	7.31	7.63	8.48	14.10	18.13	18.93	21.04	34.91	
180	0.8210	7.10	7.46	8.26	13.60	17.62	18.49	20.48	33.75	
200	0.8052	7.08	7.39	8.17	13.14	17.56	18.32	20.27	32.38	
d-Methylbenzylcarbinyl n-Octoate, $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_{15}$.										
20°	0.9420	+10.67°	+11.36°	+12.76°	+21.42°	+27.95°	+29.76°	+33.35°	+56.11°	
40	0.9261	9.85	10.53	11.86	19.95	25.80	27.58	31.07	52.25	
60	0.9105	9.20	9.81	11.00	18.49	24.12	25.70	28.80	48.46	
80	0.8946	8.69	9.25	10.42	17.31	22.78	24.25	27.30	45.34	
100	0.8787	8.14	8.76	9.82	16.30	21.32	22.96	25.73	42.64	
120	0.8626	7.74	8.27	9.34	15.42	20.29	21.66	24.47	40.40	
140	0.8467	7.59	8.00	8.97	14.90	19.89	20.97	23.52	39.04	
160	0.8306	7.44	7.82	8.72	14.40	19.49	20.50	22.83	37.72	
180	0.8150	7.31	7.67	8.46	14.02	19.05	20.09	22.18	36.71	
200	0.7990	7.26	7.67	8.30	13.83	19.02	20.10	21.74	36.23	
d-Methylbenzylcarbinyl n-Nonoate, $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_{17}$.										
20°	0.9377	+10.50°	+10.96°	+12.41°	+20.90°	+28.97°	+30.26°	+34.24°	+57.71°	
40	0.9218	9.84	10.34	11.65	19.63	27.15	28.53	32.15	54.19	
60	0.9061	9.16	9.64	10.85	18.22	25.28	26.60	29.95	50.27	
80	0.8901	8.62	8.99	10.22	17.05	23.79	24.80	28.21	47.07	
100	0.8744	8.21	8.49	9.61	16.08	22.67	23.42	26.52	44.39	
120	0.8585	8.00	8.21	9.26	15.38	22.09	22.67	25.56	42.43	
140	0.8427	7.77	8.01	8.96	14.71	21.45	22.11	24.73	40.61	
160	0.8269	7.56	7.80	8.71	14.17	20.85	21.53	24.03	39.11	
180	0.8110	7.28	7.56	8.38	13.61	20.04	20.86	23.14	37.57	
200	0.7950	7.04	7.23	8.08	13.17	19.44	19.96	22.32	36.17	
d-Methylbenzylcarbinyl n-Decoate, $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_{19}$.										
20°	0.9310	+10.13°	+10.74°	+12.20°	+20.31°	+29.38°	+31.16°	+35.56°	+58.88°	
40	0.9158	9.44	10.10	11.47	19.11	27.39	29.29	33.25	55.42	
60	0.9005	8.81	9.50	10.88	17.92	25.55	27.54	31.56	51.95	
80	0.8851	8.23	8.85	10.21	16.76	23.85	25.66	29.69	48.60	
100	0.8697	7.78	8.32	9.55	15.63	22.57	24.17	27.71	45.34	
120	0.8545	7.43	7.92	9.04	14.79	21.55	22.97	26.23	42.89	
140	0.8391	7.27	7.63	8.70	14.30	21.08	22.12	25.23	41.47	
160	0.8237	7.20	7.53	8.49	13.90	20.87	21.83	24.56	40.31	
180	0.8082	7.18	7.46	8.29	13.61	20.81	21.64	24.04	39.45	
200	0.7930	7.19	7.44	8.27	13.46	20.84	21.58	23.99	38.04	

TABLE III. (continued).

d-MethylbenzylcarbinyI *n*-Undecate, $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{O}\cdot\text{CO}\cdot\text{C}_{10}\text{H}_{21}$.

mp.	D_D^{25}	$[\alpha]_D^{25}$	$[\alpha]_D^{20}$	$[\alpha]_D^{15}$	$[\alpha]_D^{10}$	$[\alpha]_D^{5}$	$[\alpha]_D^{0}$	$[\alpha]_D^{25}$	$[\alpha]_D^{20}$	$[\alpha]_D^{15}$	$[\alpha]_D^{10}$	$[\alpha]_D^{5}$	$[\alpha]_D^{0}$
0°	0.9270	+9.92°	+10.51°	+11.81°	+20.01°	+30.17°	+31.95°	+36.14°	+60.82°				
10	0.9120	9.31	9.90	11.19	18.69	28.30	30.10	34.03	56.83				
20	0.8970	8.80	9.26	10.48	17.39	26.74	28.16	31.85	52.86				
30	0.8820	8.23	8.73	9.69	16.36	25.02	26.55	29.47	49.74				
40	0.8670	7.76	8.30	9.16	15.51	23.60	25.24	27.84	47.15				
50	0.8520	7.37	7.84	8.80	14.79	22.42	23.84	26.77	44.96				
60	0.8367	7.03	7.48	8.40	14.08	21.36	22.75	25.55	42.81				
70	0.8219	6.81	7.18	8.07	13.53	20.71	21.83	24.52	41.13				
80	0.8069	6.69	7.06	7.93	12.94	20.34	21.48	24.12	39.34				
90	0.7920	6.69	7.07	7.83	12.76	20.34	21.50	23.80	38.31				

d-MethylbenzylcarbinyI *n*-Dodecate, $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{O}\cdot\text{CO}\cdot\text{C}_{11}\text{H}_{23}$.

20°	0.9230	+9.66°	+10.11°	+11.38°	+19.39°	+30.70°	+32.17°	+56.17°	+61.67°				
40	0.9078	9.11	9.44	10.60	18.04	28.98	30.01	33.71	57.37				
60	0.8930	8.45	8.84	9.96	16.80	26.87	28.13	31.69	53.40				
80	0.8778	8.02	8.37	9.39	15.90	25.54	26.63	29.85	50.64				
100	0.8630	7.55	7.88	8.90	15.13	24.02	25.05	28.30	48.10				
20	0.8478	7.17	7.49	8.44	14.28	22.80	23.82	26.85	45.38				
40	0.8325	6.85	7.15	8.11	13.54	21.77	22.73	25.78	43.06				
60	0.8174	6.60	6.89	7.82	12.84	21.01	21.91	24.90	40.85				
80	0.8023	6.45	6.61	7.58	12.40	20.52	21.00	24.09	39.43				
100	0.7873	6.30	6.48	7.30	12.13	20.03	20.60	23.22	38.57				

d-MethylbenzylcarbinyI *Myristate*, $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{O}\cdot\text{CO}\cdot\text{C}_{13}\text{H}_{27}$.

20°	0.9196	+9.22°	+9.68°	+11.28°	+19.25°	+31.91°	+33.49°	+39.02°	+66.61°				
40	0.9044	8.52	9.06	10.17	17.18	29.50	31.37	35.20	59.44				
60	0.8890	7.99	8.19	9.23	15.63	27.64	28.33	31.96	54.11				
80	0.8740	7.55	7.94	8.78	14.76	26.13	27.12	30.37	51.07				
100	0.8589	7.19	7.51	8.50	13.99	24.90	25.98	29.41	48.42				
120	0.8436	6.88	7.22	8.17	13.40	23.79	24.99	28.26	46.35				
140	0.8287	6.54	6.90	7.82	12.85	22.63	23.89	27.05	44.46				
160	0.8132	6.27	6.55	7.48	12.24	21.69	22.68	25.86	42.34				
180	0.7978	5.98	6.22	7.14	11.76	20.68	21.51	24.73	40.68				
200	0.7826	5.75	6.01	6.90	11.23	19.90	20.78	23.88	38.87				

d-MethylbenzylcarbinyI *Palmitate*, $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{O}\cdot\text{CO}\cdot\text{C}_{15}\text{H}_{31}$.

20°	0.9130	+8.44°	+9.04°	+10.04°	+17.10°	+31.59°	+33.83°	+37.57°	+63.97°				
40	0.8984	8.01	8.35	9.36	16.04	29.97	31.23	35.01	59.99				
60	0.8836	7.55	7.87	8.75	15.00	28.23	29.42	32.72	56.08				
80	0.8690	7.02	7.31	8.23	13.81	26.25	27.33	30.77	51.55				
100	0.8541	6.60	6.89	7.74	13.05	24.69	25.78	28.94	48.81				
120	0.8395	6.31	6.60	7.35	12.32	23.61	24.68	27.49	46.09				
140	0.8249	6.03	6.33	6.97	11.74	22.54	23.67	26.07	43.93				
160	0.8101	5.80	6.10	6.73	11.36	21.70	22.80	25.16	42.47				
180	0.7952	5.66	5.85	6.51	11.12	21.16	21.87	24.36	41.59				
200	0.7805	5.52	5.73	6.28	11.09	20.65	21.42	23.48	41.50				

d-MethylbenzylcarbinyI *Stearate*, $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{O}\cdot\text{CO}\cdot\text{C}_{17}\text{H}_{35}$.

20°	0.9120	+7.92°	+8.37°	+9.44°	+15.99°	+31.82°	+33.62°	+37.95°	+64.25°				
40	0.8966	7.37	7.78	8.62	14.72	29.63	31.30	34.65	59.19				
60	0.8815	6.95	7.26	7.99	13.59	27.96	29.18	32.10	54.64				
80	0.8660	6.47	6.71	7.62	12.68	25.99	26.98	30.63	50.97				
100	0.8506	6.11	6.40	7.27	12.10	24.58	25.71	29.20	48.62				
120	0.8353	5.82	6.12	6.92	11.49	23.38	24.59	27.86	46.19				
140	0.8200	5.61	5.84	6.71	11.05	22.55	23.48	26.97	44.41				
160	0.8048	5.44	5.72	6.46	10.69	21.88	22.98	25.97	42.95				
180	0.7896	5.32	5.67	6.38	10.59	21.38	22.41	25.65	42.56				
200	0.7741	5.30	5.59	6.43	10.66	21.29	22.49	25.86	42.85				

TABLE IV.
Determinations of the Rotatory Power of d-Methylbenzylcarbinyl Acetate in (approx.) 5 per cent. Solution in Different Solvents.

Solvent.	Length Weight of obser. of tube. dissolved. cm. Grams.	α_D .	α_{gr} .	α_{re} .	α_{gr} .	α_{re} .	α_{gr} .	α_{re} .	$[\alpha]_{D_0}$.	$[\alpha]_{gr}$.	$[\alpha]_{re}$.	$[M]_{D_0}$.	$[M]_{gr}$.	$[M]_{re}$.	$[M]_{D_0}$.
Benzene	22	1.0438	+1.02°	+1.09°	+1.17°	+2.09°	+8.88°	+9.49°	+10.19°	+18.20°	+16.81°	+16.90°	+18.13°	+32.39°	
Chloroform ..	20	1.1402	0.96	1.04	1.14	1.94	8.42	9.12	10.00	17.02	14.99	16.24	17.80	30.29	
Ethyl alcohol	"	1.1608	0.93	1.00	1.10	1.83	8.01	8.61	9.47	15.72	14.26	15.33	16.86	27.99	
Ethyl acetate	"	1.1225	0.83	0.87	1.00	1.62	7.39	7.75	8.91	14.42	13.18	13.79	15.85	25.67	
Pyridine	"	1.1703	-0.19	-0.19	-0.24	-0.55	-1.62	-1.62	-2.05	-4.70	-2.89	-2.89	-3.65	-8.37	
Carbon disulphide	22	1.0120	-0.91	-0.96	-1.16	-2.51	-8.17	-8.63	-10.42	-22.55	-14.55	-15.36	-18.56	-40.15	

All solutions for the observations of rotatory power recorded in this paper were prepared by making up about 1 gram of the substance to 20 c.c. with the solvent of the laboratory, at which temperature all observations were also made.

TABLE V.
Determinations of Rotatory Power in (approx.) 5 per cent. Ethylalcoholic Solution.

Ester.	Length of observed tube, cent.	Weight of substance, grams.	α_D^{20}	α_D^{25}	α_D^{30}	$[\alpha]_D^{20}$	$[\alpha]_D^{25}$	$[\alpha]_D^{30}$	$[\alpha]_D^{20}$	$[\alpha]_D^{25}$	$[\alpha]_D^{30}$	$[\alpha]_D^{20}$	$[\alpha]_D^{25}$	$[\alpha]_D^{30}$
Acetate	20	1.1608	+0.93°	+1.00°	+1.10°	+8.01°	+8.61°	+9.47°	+15.72°	+14.28°	+15.33°	+16.86°	+16.44°	+17.08°
Propionate ..	"	1.0628	0.77	0.81	0.91	1.50	7.24	7.62	8.56	14.11	13.91	14.63	16.44	27.10
Butyrate	"	1.0288	1.25	1.31	1.49	2.47	12.14	12.74	14.48	24.01	25.02	26.23	29.84	49.45
Valerate	22	1.1266	1.82	1.95	2.13	3.62	14.70	15.75	17.20	29.23	32.33	34.64	37.84	64.31
Hexoate	20	1.1205	1.63	1.74	1.90	3.20	14.55	15.53	16.96	28.57	34.06	36.35	39.70	66.85
Heptoate ..	"	1.0475	1.58	1.61	1.85	3.14	15.09	15.38	17.67	29.98	37.43	38.14	43.82	74.37
Octoate	"	1.0715	1.57	1.61	1.84	3.14	14.66	15.03	17.18	29.32	38.41	39.39	45.01	76.81
Nonoate	"	1.1095	1.59	1.69	1.94	3.20	14.34	15.24	17.50	28.85	39.58	42.07	48.28	79.64
Decoate	"	1.1045	1.58	1.67	1.87	3.17	14.32	15.13	16.93	28.72	41.52	43.87	49.12	83.30
Undecoate ..	"	1.0500	1.43	1.49	1.70	2.91	13.61	14.19	16.19	27.71	41.40	43.15	49.21	84.26
Dodecoate ...	"	1.0375	1.35	1.40	1.63	2.72	13.02	13.60	15.71	26.23	41.39	42.92	49.08	83.41
Myristate ...	"	1.0911	1.34	1.44	1.58	2.70	12.28	13.20	14.48	24.75	42.30	45.67	50.12	85.65
Palmitate ...	"	1.0853	1.22	1.30	1.47	2.52	11.25	11.98	13.55	23.23	42.07	44.81	50.67	86.88
Stearate	"	1.0054	1.05	1.10	1.28	2.13	10.45	10.95	12.74	21.19	42.01	44.00	51.21	85.21

TABLE VI.
Determinations of Rotatory Power in (approx.) 5 per cent. Solution in Carbon Disulphide.

Ester.	Length of observed tube, cm.	Weight of sub- stance, Grams.	α_D^{20}	α_D^{25}	α_D^{30}	α_D^{35}	$[\alpha]_D^{20}$	$[\alpha]_D^{25}$	$[\alpha]_D^{30}$	$[\alpha]_D^{35}$	$[M]_D^{20}$	$[M]_D^{25}$	$[M]_D^{30}$	$[M]_D^{35}$
Acetate	22	1.0120	-0.91°	-0.96°	-1.16°	-2.51°	-8.17°	-14.62°	-10.42°	-16.56°	-15.36°	-18.56°	-15.36°	-40.16°
Propionate...	20	1.0334	-1.43	-1.51	-1.74	-3.57	-13.78	-8.42	-16.85	-26.46	-28.07	-32.34	-32.34	-66.37
Butyrate	"	1.0811	-0.84	-0.91	-1.05	-2.41	-7.77	-8.42	-9.71	-22.29	-16.01	-17.34	-20.01	-45.93
Valerate	22	0.7294	-0.37	-0.39	-0.49	-1.14	-4.61	-4.86	-6.11	-14.21	-10.15	-10.69	-13.44	-31.26
Hexoate	"	1.0043	-0.36	-0.44	-0.51	-1.21	-3.26	-3.98	-4.62	-10.95	-7.63	-9.32	-10.80	-25.64
Heptoate ..	"	1.0080	-0.20	-0.25	-0.31	-0.90	-1.80	-2.25	-2.80	-8.12	-4.47	-5.59	-6.94	-20.13
Octoate	"	1.1075	-0.11	-0.12	-0.14	-0.68	-0.90	-0.98	-1.15	-5.57	-2.36	-2.57	-3.00	-14.59
Nonoate	20	1.0997	-0.04	-0.05	-0.08	-0.49	-0.36	-0.45	-0.73	-4.45	-1.00	-1.25	-2.01	-12.29
Decoate	22	1.0804	-0.04	-0.06	-0.12	-0.47	-0.33	-0.50	-1.00	-3.92	-0.97	-1.45	-2.90	-11.37
Undecoate ...	20	1.0541	±0.00	-0.02	-0.03	-0.37	±0.00	-0.19	-0.23	-3.51*	±0.00	-0.58	-0.86	-10.68
Dodecoate ...	22	1.1118	+0.01	-0.01	-0.04	-0.33	+0.08	-0.08	-0.33	-2.70	+0.26	-0.26	-1.04	-8.58
Myristate ...	"	1.0505	+0.03	±0.00	-0.02	-0.21	+0.26	±0.00	-0.17	-1.82	+0.90	±0.00	-0.60	-6.29
Palmitate ...	20	1.0544	+0.04	+0.02	-0.01	-0.18	+0.38	+0.19	-0.09	-1.71	+1.40	+0.70	-0.35	-6.39
Stearate	22	1.1825	+0.07	+0.04	+0.03	-0.17	+0.54	+0.31	+0.23	-1.31	+2.16	+1.24	+0.93	-5.25

*Observations of Density, D_4^{20} , and Rotatory Power ($\alpha_{100 \text{ mm.}}$)
in the Homogeneous State.*

Temp.	17.5°	51.5°	94°	123°		
Density ...	1.0058	0.9774	0.9359	0.9069		
Temp.	20°	40°	73°	84°	92°	122°
α_D ...	+6.68°	+5.44°	+3.44°	+2.86°	+2.56°	+1.44°
Temp.	20°	43°	58°	76°	123°	135°
$\alpha_{D, \text{yellow}}$...	+0.40°	+5.04°	+4.16°	+3.10°	+1.36°	+0.96°
Temp.	20°	41°	73°	83°	94°	123°
α_D ...	+7.54°	+5.98°	+3.88°	+3.36°	+2.72°	+1.48°
Temp.	20°	41°	70°	82°	93°	123°
α_D ...	+12.08°	+9.40°	+6.08°	+5.00°	+4.00°	+1.76°

d-Methylbenzylcarbiny l Propionate.

Temp.	20°	56°	92°	128°		
Density ...	0.9889	0.9573	0.9242	0.8897		
Temp.	22°	51°	59°	84°	111°	187°
α_D ...	+4.88°	+3.38°	+3.20°	+2.18°	+1.58°	+1.02°
Temp.	22°	59°	85°	112°	141°	187°
$\alpha_{D, \text{yellow}}$...	+4.66°	+3.00°	+2.00°	+1.50°	+1.02°	+0.50°
Temp.	22°	52°	60°	82°	111°	187°
α_D ...	+5.42°	+3.68°	+3.40°	+2.44°	+1.66°	+1.00°
Temp.	22°	50°	60°	81°	111°	190°
α_D ...	+8.38°	+5.58°	+4.94°	+3.46°	+2.10°	+1.00°

d-Methylbenzylcarbiny l n-Butyrate.

Temp.	20.5°	58°	96°	129°		
Density ...	0.9741	0.9417	0.9078	0.8782		
Temp.	25°	48°	73°	100°	125°	169°
α_D ...	+8.44°	+7.28°	+6.34°	+5.70°	+4.98°	+4.24°
Temp.	25°	47°	64°	100°	123°	170°
$\alpha_{D, \text{yellow}}$...	+7.98°	+6.96°	+6.36°	+5.44°	+4.86°	+4.14°
Temp.	25°	49°	73°	100°	123°	169°
α_D ...	+9.50°	+8.16°	+7.18°	+6.34°	+5.68°	+4.72°
Temp.	25°	47°	73°	100°	123°	170°
α_D ...	+15.48°	+13.40°	+11.58°	+9.98°	+8.72°	+7.30°

d-Methylbenzylcarbiny l n-Valerate.

Temp.	21°	57°	99°	144°		
Density ...	0.9630	0.9340	0.8988	0.8568		
Temp.	25°	49°	71°	107°	150°	181°
α_D ...	+10.60°	+9.40°	+8.38°	+7.38°	+6.00°	+5.76°
Temp.	25°	49°	73°	118°	150°	181°
$\alpha_{D, \text{yellow}}$...	+10.14°	+9.00°	+7.96°	+6.72°	+5.82°	+5.58°
Temp.	25°	49°	71°	107°	150°	181°
α_D ...	+12.00°	+10.52°	+9.30°	+8.14°	+6.80°	+6.50°
Temp.	25°	49°	71°	105°	149°	181°
α_D ...	+19.96°	+17.74°	+15.52°	+13.38°	+10.84°	+10.20°

d-Methylbenzylcarbiny l n-Hexoate.

Temp.	18°	55.5°	89°	132°		
Density	0.9583	0.9259	0.8995	0.8622		
Temp.	30°	69°	90°	112°	157°	191°
α_D	+9.48°	+7.90°	+7.48°	+6.02°	+6.10°	+5.68°
Temp.	25°	38°	69°	85°	129°	156°
α_{yellow}	+10.40°	+9.70°	+8.36°	+7.86°	+6.94°	+6.32°
Temp.	25°	38°	69°	86°	129°	158°
α_{gr}	+11.60°	+10.84°	+9.46°	+8.88°	+7.80°	+7.06°
Temp.	25°	38°	69°	84°	129°	159°
α_{ri}	+10.30°	+17.90°	+15.40°	+14.58°	+12.62°	+11.40°

d-Methylbenzylcarbiny l n-Heptoate.

Temp.	20°	63°	96°	122°		
Density	0.9475	0.9141	0.8885	0.8655		
Temp.	24°	48°	69°	98°	135°	171°
α_D	+9.98°	+9.00°	+8.40°	+7.40°	+6.60°	+5.94°
Temp.	24°	48°	70°	98°	133°	170°
α_{yellow}	+10.58°	+9.38°	+8.74°	+7.60°	+6.90°	+6.24°
Temp.	24°	48°	70°	98°	132°	170°
α_{gr}	+11.84°	+10.60°	+9.76°	+8.58°	+7.74°	+6.92°
Temp.	24°	48°	69°	98°	131°	170°
α_{ri}	+10.72°	+17.52°	+16.10°	+14.10°	+12.78°	+11.46°

d-Methylbenzylcarbiny l n-Octoate.

Temp.	19°	59°	95°	120°		
Density	0.9424	0.9117	0.8826	0.8626		
Temp.	23°	57°	70.5°	116°	149°	180°
α_D	+9.92°	+8.48°	+8.10°	+6.68°	+6.36°	+5.96°
Temp.	23°	57°	70.5°	116°	148°	179°
α_{yellow}	+10.52°	+9.02°	+8.60°	+7.22°	+6.68°	+6.24°
Temp.	23°	58°	70.5°	116°	148°	179°
α_{gr}	+11.88°	+10.14°	+9.62°	+8.16°	+7.50°	+6.90°
Temp.	23°	57°	70.5°	118°	148°	179°
α_{ri}	+10.86°	+17.06°	+16.04°	+13.38°	+12.38°	+11.42°

d-Methylbenzylcarbiny l n-Nonoate.

Temp.	19°	56°	95.5°	139°		
Density	0.9370	0.9104	0.8777	0.8435		
Temp. 22°	51.5°	65°	98°	118°	164°	175°
α_D	+9.76°	+8.66°	+8.08°	+7.22°	+6.94°	+6.14°
Temp. 22°	49°	57°	69°	100°	118°	131°
α_{ye} +10.20°	+9.22°	+8.80°	+8.40°	+7.42°	+7.08°	+6.92°
Temp. 22°	50°	57°	70°	102°	118°	131°
α_{gr} +11.52°	+10.32°	+9.90°	+9.50°	+8.32°	+8.06°	+7.74°
Temp. 22°	48°	57°	68°	105°	118°	131°
α_{ri} +19.42°	+17.40°	+16.72°	+15.90°	+13.82°	+13.36°	+12.76°

d-Methylbenzylcarbinyll n-Decoate.

Temp.	18°	52°	94°	131°		
Density	0.9322	0.9069	0.8759	0.8462		
Temp.	27°	62°	85°	143°	176°	
α_D	+9.14°	+7.89°	+7.16°	+6.06°	+5.84°	
Temp.	27°	61°	87°	143°	150°	175°
α_{yellow}	+9.70°	+8.48°	+7.60°	+6.40°	+6.34°	+6.04°
Temp.	27°	62°	87°	143°	151°	175°
α_{cr}	+11.02°	+9.72°	+8.76°	+7.26°	+7.14°	+6.74°
Temp.	27°	58°	87°	143°	150°	175°
α_{vi}	+18.40°	+16.26°	+14.38°	+11.92°	+11.76°	+11.10°

d-Methylbenzylcarbinyll n-Undecoate.

Temp.	21°	62°	96°	133.5°		
Density	0.9255	0.8964	0.8695	0.8413		
Temp.	23°	56°	70°	83°	131°	181°
α_D	+9.10°	+8.00°	+7.66°	+7.20°	+6.08°	+5.38°
Temp.	23°	56°	63°	82°	130°	182°
α_{yellow}	+9.62°	+8.46°	+8.14°	+7.64°	+6.44°	+5.68°
Temp.	23°	56°	63°	82°	130°	182°
α_{cr}	+10.88°	+9.60°	+9.24°	+8.48°	+7.26°	+6.36°
Temp.	23°	56°	64°	80°	130°	183°
α_{vi}	+18.30°	+15.86°	+15.38°	+14.40°	+12.16°	+10.46°

d-Methylbenzylcarbinyll n-Dodecoate.

Temp.	20°	60.5°	96°	127°		
Density	0.9229	0.8925	0.8655	0.8427		
Temp.	21°	45°	63°	94°	137°	180°
α_D	+8.86°	+7.96°	+7.46°	+6.68°	+5.78°	+5.20°
Temp.	21°	49°	62°	95°	133°	182°
α_{yellow}	+9.30°	+8.26°	+7.76°	+6.94°	+6.12°	+5.28°
Temp.	21°	50°	62°	95°	130°	180°
α_{cr}	+10.46°	+9.20°	+8.88°	+7.86°	+6.90°	+6.06°
Temp.	21°	49°	62°	95°	132°	182°
α_{vi}	+17.82°	+15.66°	+14.84°	+13.30°	+11.56°	+9.90°

d-Methylbenzylcarbinyll Myristate.

Temp.	23.5°	59.5°	98°	129°		
Density	0.9138	0.8934	0.8593	0.8377		
Temp.	31°	62°	113°	182°		
α_D	+8.06°	+7.06°	+5.94°	+4.78°		
Temp.	30°	62°	114°	180°		
α_{yellow}	+8.48°	+7.22°	+6.20°	+4.96°		
Temp.	30°	62°	113°	180°		
α_{cr}	+9.74°	+8.14°	+7.06°	+5.70°		
Temp.	30°	62°	113°	180°		
α_{vi}	+16.46°	+13.74°	+11.58°	+9.34°		

d-MethylbenzylcarbinyI Palmitate

Temp.	19°	61°	99°	147°		
Density	0.9131	0.8841	0.8551	0.8199		
Temp.	22°	60°	84°	122°	169°	183°
α_D	+7.66°	+6.74°	+5.98°	+5.23°	+4.60°	+4.44°
Temp.	22°	60°	81°	117°	168°	183°
α_{yellow}	+8.00°	+7.00°	+6.26°	+5.58°	+4.82°	+4.64°
Temp.	22°	60°	80°	117°	168°	183°
α_{gr}	+9.08°	+7.76°	+7.14°	+6.26°	+5.36°	+5.14°
Temp.	22°	60°	82°	117°	168°	183°
α_{vi}	+15.43°	+13.30°	+11.84°	+10.48°	+9.12°	+8.78°

d-MethylbenzylcarbinyI Stearate.

Temp.	26.5°	59°	90°	138°		
Density	0.9058	0.8828	0.8577	0.8224		
Temp.	26°	82°	76°	104°	132°	180°
α_D	+7.00°	+6.18°	+5.68°	+5.14°	+4.74°	+4.22°
Temp.	27°	49°	75°	104°	131°	179°
α_{yellow}	+7.40°	+6.70°	+5.90°	+5.36°	+4.90°	+4.44°
Temp.	27°	53°	75°	104°	130°	179°
α_{gr}	+8.28°	+7.20°	+6.72°	+6.12°	+5.60°	+5.02°
Temp.	27°	51°	75°	104°	132°	179°
α_{vi}	+14.10°	+12.42°	+11.20°	+10.26°	+9.26°	+8.33°

The authors desire to express their thanks to Mr. John Ranson for able help in the preparation of the optically active carbinol, and to the Government Grant Committee of the Royal Society for grants which have defrayed some of the expense of this investigation.

MUNICIPAL TECHNICAL SCHOOL,
BLACKBURN.

CCXI.—*The Constituents of the Flowers of Matricaria Chamomilla.*

By FREDERICK BELDING POWER and HENRY BROWNING, jun.

THE flower-heads of the composite plant *Matricaria Chamomilla*, Linné, commonly designated as the "German Chamomile," are used to a considerable extent medicinally, and possess properties similar to those of the so-called Roman or English chamomile (from *Anthemis nobilis*, Linné). They are recognised by most of the national Pharmacopœias, but not by the British.

The older investigations of *Matricaria* flowers have indicated, besides a relatively small proportion of essential oil, the presence

of only the common constituents of plants, or, in addition thereto, the very indefinite products termed "anthermic acid" and "anthemidin," which need not be further considered here.

Klobb, Garnier, and Ehrwein (*Bull. Soc. chim.*, 1910, [iv], 7, 946) isolated from the flowers of *Matricaria* a hydrocarbon (m. p. 52–54°), to which they assigned the formula $C_{29}H_{60}$. Klobb (*Ann. chim. Phys.*, 1911, [viii], 24, 410) subsequently obtained from the same source a product melting at 120–131°, which gave the colour reaction of the phytosterols, and was regarded by him as a mixture of substances of this class. It was stated to yield an acetylated product, melting at 150–175°, from which two bromo-derivatives, melting at 158–165° and 115–118° respectively, were obtained.

Inasmuch as the present authors have recently investigated the constituents of the flowers of *Anthemis nobilis* (this vol., p. 1829), it was deemed of interest, for the purpose of comparison, also to subject the flowers of *Matricaria Chamomilla* to a complete chemical examination. The results of the present research are summarised at the end of this paper.

EXPERIMENTAL.

The material employed for this investigation consisted of a good quality of commercial "German Chamomile Flowers" from *Matricaria Chamomilla*, Linné.

Fifteen grams of the ground material were extracted with Prolli's fluid, and the resulting product tested with the usual alkaloid reagents, but only very slight reactions were obtained.

Twenty grams of the ground material were successively extracted with various solvents in a Soxhlet apparatus, when the following amounts of extract, dried in a water oven, were obtained:

Petroleum (b. p. 35–50°)	extracted 0.63 gram	= 3.15 per cent.
Ether	0.98 "	= 4.90 " "
Chloroform	0.20 "	= 1.00 " "
Ethylacetate	1.02 "	= 5.10 " "
Alcohol	3.10 "	= 15.50 " "

Total 5.93 grams = 29.65 per cent.

For the purpose of a complete examination, 22.23 kilograms of the ground flowers were completely extracted with hot alcohol, when, after the removal of the greater part of the solvent, 8.53 kilograms of a soft, green extract were obtained.

The entire amount of the alcoholic extract was mixed with a little water and distilled in a current of steam, when 23 grams of an essential oil were obtained, which possessed the characteristic, deep blue colour. The oil distilled over a wide range of tempera-

ture, the whole of the distillate being blue, with the exception of a small fraction of high boiling point (250—270°/15 mm.), which was a dark green, viscous liquid. The blue oil gave the colour reaction for furfuraldehyde, and, on keeping for some time, deposited a very small amount of a crystalline substance, which was collected. This substance melted at 110°, developed a coumarin-like odour on heating, and its solution in concentrated sulphuric acid showed a blue fluorescence. It evidently consisted of umbelliferone methyl ether, which was subsequently obtained in much larger amount, as described below. A portion of the essential oil, in ethereal solution, was shaken with aqueous sodium carbonate, when a trace of substance was removed, which, when crystallised from dilute alcohol, melted at 61°, and was evidently a fatty acid. On subsequently shaking the ethereal solution with 10 per cent. sulphuric acid, nothing definite was obtained. The oil which had been subjected to this treatment was heated for several hours with an alcoholic solution of potassium hydroxide, when only a small amount of dark coloured, acidic material was obtained, whilst the distilled neutral portion was of a much more brilliant blue colour than the original oil. This blue colour remained unchanged when the oil, in alcoholic solution, was treated with sodium.

After subjecting the alcoholic extract to distillation with steam, as above described, there remained in the distillation flask a dark brown, aqueous liquid (A), together with some fatty material, which separated on the surface, and a comparatively small amount of soft, brown resin, which was deposited. The fatty and resinous material were separately washed with hot water, then united, and constitute the product subsequently described as the resin (B), whilst the washings, after concentration, were added to the main portion of the aqueous liquid.

Examination of the Aqueous Liquid (A).

The above-mentioned aqueous liquid was concentrated under diminished pressure, and then extracted many times with ether. Both before and after this treatment it gave slight reactions with the usual alkaloid reagents. The ethereal liquid was therefore first shaken with a 5 per cent. aqueous solution of hydrogen chloride, but this removed only traces of indefinite material, and it was subsequently extracted with aqueous ammonium carbonate, sodium carbonate, and potassium hydroxide. The ammonium carbonate extract, on acidification, deposited a quantity of tarry material, which was only partly soluble in ether. The dissolved portion, after removal of the solvent, was converted into the methyl

ester, and the product distilled in a current of steam, the volatile and non-volatile portions being then treated for their separation into phenolic and non-phenolic esters. The volatile phenolic ester possessed the odour of methyl salicylate, and, after hydrolysis, yielded 0.04 gram of an acid, which crystallised in fine, colourless needles, melting at 150—151°. This acid gave a violet coloration with ferric chloride, and as no depression of the melting point ensued when mixed with salicylic acid, there was no doubt of its identity with the latter substance. The volatile, non-phenolic ester yielded on hydrolysis a small amount of acid, which was fractionally precipitated in the form of its silver salts. The latter, on ignition, gave, respectively, 44.6, 43.7, and 43.8 Ag, the first fraction of salt having undergone slight reduction. $C_8H_{15}O_2Ag$ requires $Ag=43.0$ per cent. It therefore seems probable that the volatile, non-phenolic acid consisted chiefly of an octoic acid. The portion of the esterified product which was not volatile in steam yielded nothing definite.

Isolation of Apigenin, $C_{15}H_{10}O_5$.

The above-mentioned sodium carbonate extract of the ethereal liquid was acidified, when a pale yellow substance, mixed with some tarry material, was deposited. This precipitate was collected, washed with water, and dried, when it amounted to 17.3 grams. After several separations from a mixture of alcohol and ethyl acetate, the substance was obtained as a pale yellow powder, melting at 344—347°. (Found, $C=66.0$; $H=3.9$. $C_{15}H_{10}O_5$ requires $C=66.7$; $H=3.7$ per cent.)

The substance was evidently apigenin, and its identity was further confirmed by the preparation of its acetyl (m. p. 176—178°) and benzoyl (m. p. 208°) derivatives.

The aqueous, acid liquid from which the crude apigenin had been separated, as above described, was extracted many times with ether. This removed about 0.4 gram of a substance, which, after several crystallisations from dilute alcohol, was obtained in fine, colourless needles, melting at 237—239°. On heating the substance it sublimed, and developed a coumarin-like odour. Its solution in concentrated sulphuric acid showed a strong blue fluorescence, and with ferric chloride a distinct green colour was produced. The aqueous solution of the substance possessed a slight blue fluorescence, which was not perceptible on the addition of alkali, owing to the production of a deep yellow colour. The above-described characters of the substance rendered it probable that it consisted of a mixture of umbelliferone (m. p. 225°) with

a dihydroxycoumarin, such as daphnetin or *asculetin*, since the latter compounds, which melt at 253–256° and about 270° respectively, are known to give a yellow colour with alkalis and a green coloration with ferric chloride. An analysis of the substance, and a determination of the molecular weight by the microscopic method, gave the following results:

0.0842 * gave 0.2000 CO₂ and 0.0323 H₂O. C=64.8; H=4.3.

0.0424 * in 5 c.c. of alcohol, using benzil as the standard, was between 0.045 and 0.047 mol. Mean M.W.=183.

Umbelliferone, C₉H₆O₃, requires C=66.7; H=3.7 per cent. M.W.=162.

Dihydroxycoumarin, C₉H₆O₄, requires C=60.7; H=3.4 per cent. M.W.=178.

The remainder of the substance was acetylated, and the product crystallised from water in three fractions, which possessed the following characters:

(1) M. p. 137°. Mean M.W. (in acetone solution by the microscopic method)=207.

The melting point (140°) of a known specimen of acetylumbelliferone (M.W.=204) was not depressed by admixture with this fraction, and the substances were apparently identical.

(2) M. p. 130–133°. An analysis of this fraction gave C=63.8; H=4.3.

Acetylumbelliferone, C₁₁H₈O₄, requires C=64.7; H=3.9 per cent.

Diacetyldihydroxycoumarin, C₁₃H₁₀O₆, requires C=59.5; H=3.8 per cent.

(3) M. p. 115–118°. The mean molecular weight of this fraction, in acetone solution, was 228. C₁₃H₁₀O₆ requires M.W.=262.

These results served to confirm the conclusion that the above-described substance, melting at 237–239°, consisted chiefly of umbelliferone, together with a small proportion of a dihydroxycoumarin.

Isolation of Umbelliferone Methyl Ether.

The ethereal extract of the aqueous liquid, which had been extracted with aqueous sodium carbonate, as above described, was subsequently shaken with aqueous potassium hydroxide, which removed a small amount of a crystalline substance. On finally washing and drying the ethereal liquid, and evaporating the solvent, a much larger amount of the same substance was obtained. This material was recrystallised from dilute alcohol, when it separated in flat needles of a slightly yellowish colour, melting at 115–116°.

* Dried at 110°.

The substance developed a coumarin-like odour on warming, and its solution in concentrated sulphuric acid showed a beautiful blue fluorescence. (Found, $C=68.0$; $H=4.6$. $C_{10}H_8O_3$ requires $C=68.2$; $H=4.5$ per cent.)

The above-described substance was thus identified as umbelliferone methyl ether, the occurrence of which in nature appears only once previously to have been observed, namely, in the caryophyllaceous plant *Herniaria hirsuta*, Linné (*Monatsh.*, 1889, 10, 161). The amount obtained in the present instance in a pure state was 6.3 grams, being thus equivalent to 0.028 per cent. of the weight of *Matricaria* flowers employed.

The aqueous liquid (4) which had been extracted with ether was next shaken with several successive portions of warm amyl alcohol. The combined amyl-alcoholic liquids were concentrated under diminished pressure in three stages, the material which separated during this process being in each case collected. All of these products were of a syrupy or gelatinous character, and formed on drying a varnish-like mass, which seemed to be incapable of crystallising. A portion of the material was therefore heated for two hours in dilute alcoholic solution with an amount of hydrogen chloride equal to 5 per cent. of the mixture. A resinous product was thus deposited, which was separated from the dilute alcoholic liquid, and the latter extracted with ether, but practically nothing was removed. The acid liquid was subsequently exactly neutralised with sodium carbonate, evaporated to dryness under diminished pressure, and the residue extracted with alcohol. From the product thus obtained a small amount of an osazone was prepared, which, in the crude state, melted at about 190° . The above-mentioned resinous product was distributed over purified sawdust, and the mixture extracted in a Soxhlet apparatus with ether. A yellowish substance was thus obtained, which, after separation from dilute alcohol, melted and decomposed at 345° . This substance possessed all the characters of apigenin, and its identity as such was confirmed by analysis. (Found, $C=66.3$; $H=4.2$. $C_{15}H_{10}O_5$ requires $C=66.7$; $H=3.7$ per cent.)

From these results it may be concluded that apigenin existed in the flowers of *Matricaria* in the form of a glucoside, as well as in the free state, although, in distinction from the flowers of *Anthemis nobilis* (this vol., p. 1833), the glucoside could not be obtained in a crystalline form.

After removal of the amyl alcohol from the aqueous liquid (4), a portion of the latter, representing 4 kilograms of the alcoholic extract, was treated with a slight excess of a solution of basic lead

acetate. A voluminous precipitate was thus produced, which was collected, thoroughly washed with water, then suspended in water, and decomposed by hydrogen sulphide. The filtrate from the lead sulphide was concentrated under diminished pressure, but then gave no precipitate with a solution of gelatin, and only a brown coloration with ferric chloride, thus indicating the absence of tannin. A portion of the concentrated liquid was heated with both 5 per cent. hydrochloric acid and aqueous alkali, but nothing definite was obtained by this treatment.

The filtrate from the precipitate produced by basic lead acetate was subsequently treated with hydrogen sulphide for the removal of the excess of lead, again filtered, and then concentrated under diminished pressure. The syrupy liquid so obtained (1173 grams) evidently contained a quantity of sugar, since it readily yielded *d*-phenylglucosazone, melting at 208°.

A portion of the syrupy liquid was acetylated, and from the resulting product a very small amount of a crystalline substance was isolated, which, after recrystallisation from a mixture of alcohol and ethyl acetate, separated in colourless needles, melting at 284–288°. The amount of this substance was too small to permit of its further examination. The uncrystallisable portion of the acetylated product was subsequently hydrolysed by heating with dilute sulphuric acid in a current of steam, and the acid removed by means of baryta. As the liquid so obtained was laevo rotatory, it indicated the sugar to consist, to a predominating extent, of *lævulose*.

Inasmuch as the above-mentioned syrupy liquid gave decided reactions with the usual alkaloid reagents, a portion of it was made alkaline by sodium carbonate, and subsequently extracted with both ether and chloroform, but only traces of indefinite, amorphous material were removed by these solvents.

Isolation of Choline, $C_5H_{15}O_2N$.

A quantity (480 grams) of the above-mentioned syrupy liquid was repeatedly treated with alcohol until a product was obtained which was soluble in nearly absolute alcohol. To the alcoholic solution of this product an alcoholic solution of mercuric chloride was added, the resulting precipitate being collected, and dissolved as completely as possible in hot water. The mercury was then removed from the aqueous liquid by means of hydrogen sulphide, the mixture filtered, and the filtrate, after being nearly neutralised with sodium carbonate, evaporated to dryness under diminished pressure. The residue thus obtained was extracted with alcohol, the solvent evaporated, and the residual substance dissolved in

water. To this aqueous solution, acidified with sulphuric acid, a solution of phosphotungstic acid was added, the resulting precipitate being collected, decomposed by aqueous barium hydroxide, and the mixture filtered. After the removal of the excess of barium by carbon dioxide, the filtrate was slightly acidified with hydrochloric acid, and evaporated to dryness under diminished pressure. This residue was repeatedly treated with absolute alcohol until, on the evaporation of the solvent, a product was obtained which dissolved completely in cold absolute alcohol. From one half of this solution a platinichloride was prepared, which, after crystallisation from water, melted and decomposed at 255° , and amounted to about 0.4 gram. The salt was dried at 110° and analysed. (Found, C=19.5; H=4.8; Pt=31.5. $(C_6H_{11}ONCl)_2PtCl_4$ requires C=19.5; H=4.5; Pt=31.7 per cent.)

These results established the presence of choline in *Matricaria* flowers. The amount obtained, in the form of the pure platinichloride, was equivalent to about 0.007 per cent. of the weight of flowers employed. No evidence could be obtained of the presence of any basic substance other than choline.

Examination of the Resin (B).

The combined fatty and resinous material, which had been separated from the aqueous liquid (A) after distillation of the original alcoholic extract with steam, was distributed over purified sawdust, and the thoroughly dried mixture then extracted successively in a large Soxhlet apparatus with various solvents. The material from 4 kilograms of the original alcoholic extract yielded the following amounts of the respective products, dried at 100° :

Petroleum (b. p. $35-50^{\circ}$)	extracted	350.0	grams.
Ether	"	98.0	"
Chloroform	"	12.5	"
Ethyl acetate	"	23.0	"
Alcohol	"	130.0	"
Total		613.5	grams.

Petroleum Extract of the Resin.

This extract, after the removal of the solvent, was heated with an alcoholic solution of potassium hydroxide, the greater part of the alcohol then removed, water added, and the mixture thoroughly extracted with ether. On concentrating the ethereal extract, a considerable amount of crystalline material separated, which was collected, and by the subsequent complete evaporation of the ether a further amount of substance was obtained. In order to ascertain

whether the last-mentioned product contained a fatty alcohol, it was subjected to treatment with phthalic anhydride, but with a negative result. The phthalic anhydride having then been removed from the material, the latter was subsequently dissolved in a large volume of alcohol.

Isolation of Triacontane, $C_{30}H_{62}$.

The alcoholic solution of the substance which had been treated with phthalic anhydride, as above described, was concentrated, and the portions of material which successively separated during this operation were separately collected. The first three of these fractions were oily, but after being distilled under a pressure of 14 mm. they were found to crystallise. This material was crystallised several times from ethyl acetate, and proved to be identical with that which had separated from the above-mentioned ethereal liquid. The substance was finally obtained in colourless, pearly leaflets, melting at $63-65^{\circ}$, and was identified as triacontane. (Found, $C=84.9$; $H=14.9$. Calc., $C=85.3$; $H=14.7$ per cent.)

The amount of this hydrocarbon obtained in a pure state was 19 grams, being thus equivalent to about 0.16 per cent. of the weight of *Matricaria* flowers employed.

Isolation of a Phytosterol, $C_{27}H_{46}O$.

The more soluble products from the above-mentioned alcoholic solution consisted chiefly of a crystalline substance, together with some oily material. The solid was separated, crystallised several times from petroleum of high boiling point, and finally from dilute alcohol. It was thus obtained in colourless leaflets, melting at $132-134^{\circ}$, which gave the colour reaction of the phytosterols:

0.0945, on heating at 105° , lost 0.0039 H_2O . $H_2O=4.1$.

0.0906 * gave 0.2797 CO_2 and 0.0972 H_2O . $C=84.2$; $H=11.9$.

$C_{27}H_{46}O, H_2O$ requires $H_2O=4.5$ per cent.

$C_{27}H_{46}O$ requires $C=83.9$; $H=11.9$ per cent.

This substance was thus identified as a phytosterol. A portion of it was converted into an acetyl derivative, which, after crystallisation from a mixture of alcohol and ethyl acetate, separated in glistening leaflets, melting at $122-123^{\circ}$. (Found, $C=81.1$; $H=11.2$. $C_{27}H_{46}O \cdot CO \cdot CH_3$ requires $C=81.3$; $H=11.2$ per cent.)

Examination of the Fatty Acids.

The alkaline, aqueous liquid resulting from the hydrolysis of the petroleum extract of the resin, which had been extracted with

* Anhydrous substance.

ether for the removal of the unsaponifiable material, was acidified and again extracted with ether. The fatty acids thus obtained were converted into their ethyl esters, and the latter distilled in a current of steam. A small amount of volatile esters was thus obtained, which possessed an agreeable, fruity odour, but when redistilled they passed over indefinitely between 100° and 250°, and thus consisted of a complex mixture.

The main portion of the esterified product, which was not volatile in steam, was distilled several times under diminished pressure, when it finally passed over between 200° and 260°/12 mm., and amounted to 140 grams. These esters were hydrolysed, and the acids so obtained separated into liquid and solid portions by conversion into their lead salts, and treatment of the latter with ether.

The Liquid Acids.—These acids distilled between 200° and 240°/14 mm., and amounted to 25 grams. They had an iodine value of 132·6, and, on analysis, gave C=76·7; H=11·5.

$C_{18}H_{34}O_2$ requires C=76·6; H=12·1 per cent. I.V.=90·1.

$C_{18}H_{32}O_2$ " C=77·1; H=11·4 " " I.V.=181·4.

The above results indicate the liquid acids to have consisted of a mixture of oleic and linolic acids in about equal proportions.

The Solid Acids.—These acids, when distilled under diminished pressure, passed over between 230° and 260°/15 mm. By fractional crystallisation, about 1 gram of an acid was obtained, which melted at 77–78°, and had a neutralisation value of 135·4. This was identified as cerotic acid. (Found, C=79·1; H=13·4. $C_{27}H_{54}O_2$ requires C=79·0; H=13·2 per cent. N.V.=136·8.)

The principal portion of solid acid was separated by crystallisation into two fractions, which possessed the following characters:

(1) M. p. 54–55°. C=75·2; H=12·5. N.V.=213·4.

(2) M. p. 55–56°. C=75·5; H=12·6. N.V.=207·1.

$C_{16}H_{32}O_2$ requires C=75·0; H=12·5 per cent. N.V.=219·1.

$C_{18}H_{36}O_2$ " C=76·1; H=12·7 " " N.V.=197·5.

It would thus appear that both of the above fractions consisted of mixtures of palmitic and stearic acids, but in somewhat different proportions.

Ether Extract of the Resin.

This extract of the resin deposited a comparatively small amount of substance, which was collected, and the ethereal liquid was then shaken successively with aqueous ammonium carbonate, sodium carbonate, and potassium hydroxide. Both the first- and the last-mentioned alkali removed only a small amount of indefinite material. The sodium carbonate extract, however, on acidification,

yielded a further small amount of apigenin, and, on subsequently extracting the filtered acid liquid with ether, a very small amount of a colourless substance was obtained, which crystallised from dilute alcohol in needles, melting at about 216° . This substance appeared to be identical with that obtained in an analogous manner from the ethereal extract of the original aqueous liquid (4). After the above-described extraction of the ethereal liquid with alkalis, the ether was evaporated. The residue, which consisted chiefly of amorphous, green material, yielded a further small amount of umbelliferone methyl ether, melting at $115-117^{\circ}$.

Isolation of a Phytosterol Glucoside.

The substance deposited from the ether extract of the resin, as above noted, together with some material of a similar nature which had separated from an emulsion formed on extracting the previously described fatty acids, was brought into a Soxhlet apparatus and extracted with absolute alcohol. The product thus obtained was then separated twice from dilute pyridine, when it formed a nearly colourless, microcrystalline powder, melting and decomposing at about 285° :

0.1051 * gave 0.2795 CO_2 and 0.0983 H_2O . $\text{C}=72.5$; $\text{H}=10.4$.

A sitosterol glucoside, $\text{C}_{33}\text{H}_{56}\text{O}_6$, requires $\text{C}=72.3$; $\text{H}=10.2$ per cent.

A small portion of the substance was converted into an acetyl derivative, which crystallised in colourless leaflets, melting at $158-160^{\circ}$.

The greater part of the material was hydrolysed in amyl alcohol solution by means of hydrochloric acid (compare T., 1913, 103, 399). There was thus obtained a reducing sugar and a substance crystallising in lustrous leaflets, melting at $132-133^{\circ}$, which was identified as a phytosterol. (Found, $\text{C}=83.7$; $\text{H}=12.3$. $\text{C}_{27}\text{H}_{46}\text{O}$ requires $\text{C}=83.9$; $\text{H}=11.9$ per cent.)

It is evident from these results that the above-described substance was a phytosterol glucoside.

Chloroform, Ethyl Acetate, and Alcohol Extracts of the Resin.

The chloroform extract was shaken with aqueous alkalis, but yielded nothing definite. The ethyl acetate and alcohol extracts, when heated with sulphuric acid in aqueous alcohol, gave in each case a small amount of apigenin, together with a sugar from which an osazone, melting in the crude state at about 197° , was prepared. These two extracts, therefore appeared to contain a small amount of an apigenin extract of

* A. Dried at 105° .

Summary.

The material employed for this investigation consisted of the flower-heads of *Matricaria Chamomilla*, Linné, commonly known as the German chamomile.

In addition to a deep blue essential oil, which deposited a very small amount of umbelliferone methyl ether, the flowers were found to contain the following compounds: (1) salicylic acid, together with, apparently, an octoic acid; (2) apigenin, $C_{15}H_{10}O_5$; (3) a glucoside of apigenin, which could not be obtained in a crystalline state; (4) umbelliferone methyl ether, $C_{10}H_8O_3$, and a crystalline product (m. p. 237–239°), which possessed the characters of a mixture of umbelliferone and a dihydroxycoumarin; (5) choline, $C_5H_{15}O_2N$; (6) triacontane, $C_{30}H_{62}$; (7) a phytosterol, $C_{27}H_{46}O$; (8) a phytosterol glucoside, $C_{33}H_{56}O_6$; (9) palmitic, stearic, cerotic, oleic, and linolic acids, together with an indefinite mixture of volatile fatty acids. The flowers contained, furthermore, a quantity of sugar, which yielded *d*-phenylglucosazone, melting at 208°. The amount of fatty and resinous material, from which some of the above-mentioned substances were obtained, was equivalent to 5.9 per cent. of the weight of flowers employed.

In comparing the constituents of the flowers of *Matricaria Chamomilla* (German Chamomile) with those of the flowers of *Anthemis nobilis* (Roman or English Chamomile), which have recently been investigated by the present authors (this vol., p. 1829), it may be observed that whilst some of the compounds are common to both, there are also considerable differences.

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CCXII.—*Experiments on the Conversion of Certain
Dibromides of the Type of Ethylene Dibromide
into the Corresponding Glycols.*

By ERNEST GRAHAM BAINBRIDGE.

It has long been known that ethylene glycol can be obtained from its diacetate more readily than from ethylene dibromide. Wurtz (*Ann. Chim. Phys.*, 1859, [iii], 55, 400, 433) obtained glycol by heating glycol diacetate with alkalis, baryta, or slaked lime. Debus (*Annalen*, 1861, 119, 316) obtained glycol from ethylene

dibromide by heating it with potassium acetate, and treating the product—which he assumed to be glycol monoacetate—in a sealed tube at 100°. Kremann (*Zeitsch. Elektrochem.*, 1907, **13**, 307) has shown that glycol diacetate can be hydrolysed in dilute alcoholic solution by small quantities of alkalis, and Julius Meyer (*Zeitsch. Elektrochem.*, 1907, **13**, 186) by dilute solutions of hydrochloric acid. These experiments, however, were carried out from a physico-chemical point of view. Henry (*Bull. Acad. roy. Belg.*, 1906, 732) claims to have obtained a 90 per cent. yield of glycol by heating the diacetate with methyl alcohol containing 1.5 per cent. of hydrochloric acid.

The present author first investigated the formation of glycol from glycol diacetate with the object of finding, if possible, a better method of preparing glycol than the methods previously used. This object was attained, and a very satisfactory yield was obtained by boiling with a dilute alcoholic solution of sodium ethoxide and fractionating the product, which is more convenient than the previous method of boiling the diacetate with excess of hydrated baryta or lime, and distilling off the glycol and water in the presence of a relatively large mass of solid substance.

The success of these preliminary experiments led to an attempt to apply the same reaction to the preparation of the higher glycols.

In order to prepare the diacetates of these higher glycols, the usual method of heating the corresponding dibromides with acetates of certain metals, such as potassium and silver, was adopted. It was found to be a matter of difficulty, however, to obtain some of these diacetates, partly on account of the costliness of the dibromides and partly on account of the inefficiency of the methods of preparation. An investigation of the causes of this inefficiency showed that it was due to the formation of unsaturated bromides of the type of vinyl bromide.

Much time was spent in unsuccessful attempts to improve the said methods of preparation by the use of various metallic acetates.

In all, it was possible to obtain the diacetates of four of the higher glycols, and these have been investigated. α -Butylene glycol diacetate had to be prepared from the corresponding glycol on account of the difficulty of obtaining α -dibromobutane in sufficient quantity.

For convenience, the matter of this paper has been divided into two parts. The first part deals with the attempts to convert the dibromides into the diacetates, whilst the second part concerns the hydrolysis of such diacetates as have been obtained.

PART I.—*The Action of Metallic Acetates on Certain Dibromides.*

In order to convert a dibromide of the type of ethylene dibromide into the diacetate of its corresponding glycol, it has been usual to heat the dibromide with potassium or silver acetate in the presence of glacial acetic acid.

The author has found that by this treatment many of these dibromides yield unsaturated bromides by the elimination of hydrogen bromide, $\text{CR}_2\text{Br}\cdot\text{CHBr}\text{R} \rightarrow \text{CR}_2\text{:CRBr}$. These unsaturated bromides are homologues of vinyl bromide, $\text{CH}_2\text{:CHBr}$, and are formed in some cases as the sole product, in other cases in addition to the diacetate expected.

It is well known that the elimination of hydrogen bromide in this manner takes place with alcoholic potassium hydroxide. Solonina (*J. Russ. Phys. Chem. Soc.*, 1898, **30**, 826) has shown that this can also be brought about by means of sodium phenoxide.

The tendency to form these unsaturated bromides was found to be greater with potassium acetate than with silver acetate. Experiments were carried out with lead acetate and ethylene dibromide, but as the yield of glycol diacetate was less than that with potassium acetate, it was not considered advisable to apply it to the homologues of ethylene dibromide, which are more expensive.

The results of the present investigations are briefly as follows:

Ethylene dibromide, when heated with potassium, silver, and lead acetates, gives a nearly quantitative yield of ethylene glycol diacetate. Many attempts were made to convert it into vinyl bromide with these reagents, but without success.

Trimethylene bromide is also converted quantitatively into trimethylene glycol diacetate.

In the case of propylene bromide, about two-thirds is converted into α -bromo- Δ^1 -propylene, $\text{CHMe}\cdot\text{CHBr}$, and one-third into propylene glycol diacetate, the exact proportions depending on experimental conditions.

*iso*Butylene bromide is converted quantitatively into α -bromo- β -methyl- Δ^1 -propylene $\text{CMe}_2\cdot\text{CHBr}$.

ψ -Butylene bromide with potassium acetate gives β -bromo- ψ -butylene, $\begin{array}{c} \text{CH}_3 \\ | \\ \text{H} > \text{C} : \text{C} < \begin{array}{c} \text{Br} \\ | \\ \text{CH}_3 \end{array} \end{array}$. With silver acetate, the amount of this is smaller, but some ψ -butylene glycol diacetate is produced.

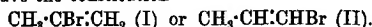
EXPERIMENTAL.

Vinyl Bromide.—Attempts were made to convert ethylene bromide into vinyl bromide, but no unsaturated compounds could

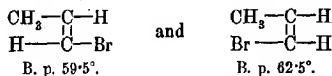
be detected in the products even when ethylene bromide was heated with potassium acetate in a sealed tube at 200°.

α-Bromo-Δ-propylene.—Fifty grams of propylene bromide were heated in a reflux apparatus (on a sand-bath) with 50 grams of fused potassium acetate and 20 grams of glacial acetic acid for about five hours. At the end of this time the mass was distilled and the distillate heated with 50 grams of propylene bromide, 60 grams of potassium acetate, and 20 grams of glacial acetic acid for four to five hours. The mass was distilled, and the distillate fractionated; 27 grams of propylene glycol diacetate were obtained, representing a yield of 35 per cent. of the theoretical.

Ethylene bromide under similar conditions yields 70 to 80 per cent. of the theoretical quantity of glycol diacetate. On investigating the cause of this small yield, it was found that the lower fractions of the distillate contained a heavy oil, insoluble in water, which contained bromine, and decolorised bromine water. It was isolated by precipitating with water, washing, drying, and carefully fractionating. After several fractionations a liquid was obtained boiling at 58–60°. An analysis of this fraction proved it to have the formula C_3H_5Br . From its mode of formation it must obviously have the constitution



The former boils at 47°, and the latter exists in two forms, namely,



On boiling with dilute sodium hydroxide, the first compound (I) would give $CH_3 \cdot C(OH) : CH_2$, which would change over into acetone. The second compound (II) would by a similar process give propaldehyde. The substance was boiled with dilute sodium hydroxide, and the product proved to contain an aldehyde. Of the two isomeric forms of (II), the substance was concluded to be the first, this agreeing better with the boiling point, and the first being the more stable form.

It appears from these experiments that the action of potassium acetate on propylene bromide produces an equilibrium mixture of propylene glycol diacetate and *α-bromo-Δ-propylene*.

The exact proportions of these substances depends on experimental conditions. On heating for two or three days, the proportion of the diacetate was smaller. In an actual experiment, 28 per cent. of the theoretical amount of the diacetate was obtained.

α-Bromo-β-methyl-Δ-propylene.—In the experiments carried out with isobutylene bromide, no trace of isobutylene glycol diacetate could be detected.

One hundred grams of isobutylene bromide were heated with 120 grams of potassium acetate and 50 c.c. of glacial acetic acid on a sand-bath for five hours. The mass was then treated with enough water to dissolve the whole of the solid matter. A heavy oil sank to the bottom, which was separated and dried. On fractionation a liquid was obtained boiling at 91–92°. An analysis of this substance indicated the formula C_4H_7Br . When boiled with dilute sodium hydroxide solution it gave an aldehyde, and was therefore concluded to be α -bromo- β -methyl- Δ^2 -propylene, the boiling point of which is 92°.

Silver acetate gave the same result as potassium acetate. An alteration in the method of isolation was necessary. Instead of adding water to the product of heating, it was distilled until all the volatile matter had passed over. The distillate was then treated with water, and the substance isolated as before.

β -Bromo- ψ -butylene and ψ -Butylene Glycol Diacetate.—Ninety grams of ψ -butylene dibromide were boiled for about eight hours with 105 grams of potassium acetate in 50 c.c. of glacial acetic acid. The product was then treated with water, and the oil separated and dried. On fractionation a liquid was obtained, which boiled at 91–93°. This corresponds with *trans*- β -bromo- ψ -butylene, which boils at 91°. The crude product weighed 33 grams, representing a yield of 66 per cent. of the theoretical. A little (about 3 grams) ψ -butylene glycol diacetate was obtained.

Silver acetate gave a comparatively good yield of ψ -butylene glycol diacetate. Fifty grams of ψ -butylene dibromide were heated with 80 grams of silver acetate and 20 c.c. of glacial acetic acid for four hours, the products distilled off, and heated with another 50 grams of dibromide, 90 grams of silver acetate, and 30 c.c. of glacial acetic acid. The products were again distilled off and carefully fractionated. About 19 grams of β -bromo- ψ -butylene were obtained, and about 25 grams of a liquid boiling at 190°. The latter was analysed, and an acetyl determination carried out, the results of which agreed with the formula $AcO \cdot CHMe \cdot CHMe \cdot OAc$. It was concluded that the liquid was *ψ -butylene glycol diacetate*, which has not previously been described. The yield of this substance was 31 per cent. of the theoretical.

Summary.

Although only five of the dibromides have been investigated, an important feature becomes apparent on classifying them according to their behaviour with potassium and silver acetates:

Ethylene bromide	}	give diacetate but no unsaturated bromide.
and		
Trimethylene bromide	}	gives some unsaturated bromide and some diacetate.
Propylene		
„		
isoButylene	„	gives unsaturated bromide but no diacetate.

The second, $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$, contains two bromine atoms attached to carbon atoms, which are separated by a CH_2 group, and this gives no unsaturated dibromide.

The last, $\text{CMe}_2\text{Br}\cdot\text{CH}_2\text{Br}$, which contains two bromine atoms attached to adjacent carbon atoms, gives no diacetate.

The third, $\text{CHMeBr}\cdot\text{CH}_2\text{Br}$, gives both the unsaturated compound and the diacetate.

In comparing the physical properties of members of the series, it frequently happens that the first member is anomalous. In this case, ethylene bromide, which contains bromine attached to adjacent carbon atoms, does not behave like the other members possessing this feature. Leaving, therefore, ethylene bromide out of consideration, the following suggestions can be put forward, namely, that (1) dibromides which have the two bromine atoms attached to adjacent carbon atoms are capable of forming unsaturated compounds, and (2) that the tendency to form the diacetate decreases as we ascend the series. On the other hand, ψ -butylene bromide, $\text{CHMeBr}\cdot\text{CHMeBr}$, gives a mixture of the diacetate and the unsaturated compound in about the same proportions as does propylene bromide. This, however, might be accounted for by the symmetry of the molecule of ψ -butylene bromide.

PART II.—*The Conversion of Diacetates into Glycols.*

The diacetates of five glycols were investigated. In the case of ethylene glycol diacetate and trimethylene glycol diacetate, the best yields were obtained by boiling with a dilute alcoholic solution of sodium ethoxide and distilling the product.

α -Butylene glycol diacetate was hydrolysed by this means, but not so readily as the previous two diacetates.

In the other two cases, propylene glycol diacetate and ψ -butylene glycol diacetate, this method was not effective.

The other hydrolytic agents tried, namely, dilute alcoholic sodium hydroxide and acetate, and aqueous sodium hydroxide and acetate, were not so effective as sodium ethoxide, and consequently were not applied to the higher glycols.

Although the above method is not general, the following gave good results with all the diacetates investigated. The diacetate was boiled with an equimolecular quantity of sodium ethoxide in

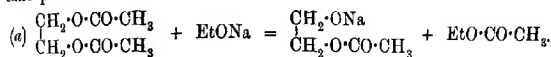
alcohol. The supernatant liquid was distilled off, and the residue saturated with carbon dioxide. The latter was then boiled with about two molecular proportions of water, and the mass distilled. On fractionation of the distillate, about 70 to 80 per cent. of the theoretical quantity of glycol could be obtained.

Sufficient evidence has not yet been obtained to determine the exact nature of this reaction, and at present the method can only be put forward as a practical method of preparation.

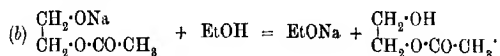
Glycol Diacetate.—This has been worked out in some detail. The following hydrolytic agents have been tried: alcoholic sodium ethoxide, sodium hydroxide, sodium acetate, and aqueous sodium hydroxide and sodium acetate. In some cases different strengths of solutions were tried.

It was found that a dilute alcoholic solution of sodium ethoxide is capable of hydrolysing glycol diacetate catalytically, forming ethyl acetate and glycol, the yield of the latter being 75 to 85 per cent. of the theoretical.

The following equations probably represent the changes which take place:



This intermediate product has not been isolated, and is probably decomposed instantly, as follows:



The remaining acetyl group will, of course, be eliminated in a similar manner.

The effect of larger quantities of sodium ethoxide was also tried. The result was the same, and the hydrolysis was effected in less time. When alcohol containing small quantities of water was used, a smaller yield of glycol was obtained, in some cases the amount being as little as 10 per cent. of the theoretical. Alcoholic solutions of sodium hydroxide were found to give a smaller yield than solutions containing an equivalent quantity of sodium ethoxide.

These last two results can be explained as follows. The solution of sodium hydroxide in absolute alcohol or sodium ethoxide in alcohol containing water would consist of an equilibrium mixture of sodium ethoxide and sodium hydroxide. As the hydrolysis took place, the sodium hydroxide would be converted into sodium acetate (which, as shown below, produces only a small amount of hydrolysis), leaving a smaller amount of sodium ethoxide than would be present if absolute alcohol and an equivalent quantity of sodium ethoxide had been used. Therefore, hydrolysis being

due to sodium ethoxide, would take place more slowly, or in the same length of time less of the ester would be hydrolysed.

Equimolecular quantities of sodium hydroxide and glycol diacetate gave, on warming, a bulky precipitate of sodium acetate, thus removing half of the acetyl radicle from solution. The rest of the acetyl radicle was eliminated, probably catalytically, for about 70 to 80 per cent. of the theoretical amount of glycol was obtained.

With regard to aqueous hydrolytic agents, it was found that glycol diacetate could be hydrolysed catalytically by means of dilute aqueous sodium hydroxide. This would be expected to form sodium acetate, and thus stop the reaction unless sodium acetate was also capable of acting catalytically in the same manner. This point was tested by heating equal quantities of glycol diacetate with solutions containing equivalent small quantities of sodium hydroxide and sodium acetate respectively. At the end of a certain time the amount of hydrolysis was tested by titrating with hydrochloric acid. This was practically the same in the two cases. This method of hydrolysis is not very suitable from a preparatory point of view, owing to the volatility of glycol in steam.

Trimethylene Glycol Diacetate.—This was found to be hydrolysed in a similar manner to glycol diacetate by dilute alcoholic sodium ethoxide and sodium hydroxide. The best results were obtained with the former, the yield being 80 per cent.

Propylene Glycol Diacetate and ψ -Butylene Glycol Diacetate.—With dilute alcoholic sodium ethoxide no hydrolysis took place, the diacetate being recovered.

α -Butylene Glycol Diacetate.—With dilute alcoholic sodium ethoxide a small amount of hydrolysis had taken place, but the product was not easy to separate from the unchanged acetate. With a molecular proportion of sodium ethoxide, 75 per cent. of the theoretical quantity of α -butylene glycol was obtained.

EXPERIMENTAL.

Glycol Diacetate.

(a) *Sodium Ethoxide.*—0.1 Gram of sodium was dissolved in 50 c.c. of absolute alcohol (distilled from calcium), and to this solution were added 7.3 grams of glycol diacetate. Immediately an odour of ethyl acetate was observed. The mixture was heated for about six hours on a steam-bath in a reflux apparatus, and then the mass was distilled. The lower fractions contained ethyl acetate and alcohol. When the temperature reached 80° the thermometer began to rise rapidly, and at 190–200° a viscous

liquid distilled over. On fractionation, the main portion boiled at 195° , and proved to be glycol. A small amount of solid residue was left, which consisted of sodium ethoxide and a little sodium acetate.

A second experiment was carried out with the object of estimating the amount of ethyl acetate. 3.154 Grams of the ester were hydrolysed as above. After the hydrolysis had taken place, the ethyl acetate and alcohol were distilled over from a steam-bath. The distillate was boiled with excess of $N/10$ -alcoholic potassium hydroxide for two hours, and then titrated with $N/10$ -hydrochloric acid. The alkali used corresponded with 28.6 c.c. of N -potassium hydroxide. 3.154 Grams of the ester, if completely hydrolysed, would require 33.5 c.c. of N -potassium hydroxide. Therefore the amount of ethyl acetate given off corresponded with 85.1 per cent. of the theoretical.

With larger quantities, a similar result was obtained. One molecular proportion gave 82.1 per cent. of ethyl acetate, and two molecular proportions gave 80 per cent.

Further experiments were carried out, using alcohol containing small amounts of water. 0.1 Gram of sodium was dissolved in 50 c.c. of alcohol, and 0.5 c.c. of water added. 14.6 Grams of ester were added, and the mixture was heated on a steam-bath for six hours. On distillation, 4.3 grams of glycol were obtained. This represents a yield of 71 per cent. of the theoretical.

In an experiment with 1 c.c. of water in 50 c.c. of absolute alcohol, 14.6 grams of glycol diacetate gave 0.6 gram of the glycol (=10 per cent.). The bulk of the ester was unchanged.

(b) *Alcoholic Sodium Hydroxide*.—Experiments were carried out with sodium hydroxide in the same way as with sodium ethoxide, using 0.17 gram of sodium hydroxide.

With absolute alcohol (50 c.c.), 7.3 grams of glycol diacetate gave 2.0 grams of glycol (=64 per cent. of the theoretical).

With absolute alcohol containing 1 per cent. of water, 14.6 grams of glycol diacetate gave 0.4 gram of glycol (=6 per cent. of the theoretical).

Two experiments were carried out under the same conditions, one using sodium hydroxide (0.17 gram) and the other the corresponding quantity of sodium ethoxide, both in absolute alcohol. The latter gave 79 per cent. of glycol, the former 64 per cent.

(c) *Aqueous Sodium Hydroxide*.—14.6 Grams of glycol diacetate were heated for fifteen minutes with 8 grams of sodium hydroxide in 50 c.c. of water. At the end of this time all the glycol diacetate had disappeared, and the solution was quite clear. The mixture was then distilled to dryness, the residue consisting

of sodium acetate. On fractionating the distillate, two fractions were obtained, one consisting of water (100° to 110°), and the other (above 190°) consisting of glycol; 3.1 grams of the latter were obtained, representing a yield of 50 per cent. of the theoretical. The former fraction was tested for glycol by the following test devised by the author. To a few drops of the substance about 1 c.c. of dilute potassium permanganate is added, and then sulphuric acid is poured down the side of the test-tube until about 2 c.c. have collected at the bottom; the mixture is then shaken. Acetic acid does not decolorise the solution, glycol diacetate decolorises it slowly, and glycol decolorises it immediately.

Glycol was found to be present in the first fraction. It appears, therefore, that the hydrolysis of glycol diacetate can be effected by this means, but a poor yield is obtained, glycol being lost in two ways, namely, through its volatility in steam and through the difficulty of separation of the last traces of glycol from the solid residue.

With dilute sodium hydroxide glycol diacetate was hydrolysed completely after heating for some time. Here, as in the last experiment, a large amount of the glycol was lost in the steam.

(d) *Alcoholic Sodium Acetate*.—7.3 Grams of glycol diacetate were heated with 0.4 gram of sodium acetate in alcoholic solution on a steam-bath for eight hours. On fractionation, 6.0 grams of the diacetate were recovered unchanged. An estimation of the ethyl acetate formed showed that 0.5 gram of the diacetate had been hydrolysed.

(e) *Aqueous Sodium Acetate*.—In order to test whether sodium acetate was capable of hydrolysing glycol diacetate catalytically to the same extent as sodium hydroxide, the following experiment was carried out. Two quantities of 14.6 grams of glycol diacetate were boiled respectively with 0.05 gram-molecule of sodium hydroxide and 0.05 gram-molecule of sodium acetate in 50 c.c. on the same sand-bath. After a time, when the hydrolysis was still incomplete, the flasks were allowed to cool. The solutions were filtered through moistened filter paper, made up to 250 c.c., and titrated with $N/10$ -potassium hydroxide. In the experiment with sodium hydroxide, 11.2 per cent. of the diacetate had been hydrolysed; in the experiment with sodium acetate, 10.8 per cent.

Trimethylene Glycol Diacetate.

0.1 Gram of sodium was dissolved in 25 c.c. of alcohol, and the resulting solution heated on a steam-bath with 8.0 grams of trimethylene glycol diacetate for twelve hours. On fractionation,

3.2 grams of trimethylene glycol were obtained, representing a yield of 80 per cent. of the theoretical.

Propylene Glycol Diacetate.

0.1 Gram of sodium was dissolved in 25 c.c. of absolute alcohol, and the solution heated on a steam-bath with 8.0 grams of propylene glycol diacetate for twelve hours. On distillation, the product (6.0 grams) consisted largely of unchanged diacetate, boiling at 183—186°. As the boiling point of propylene glycol is only 3° higher than this, it is possible that the product contained a little of the glycol. It was, however, a mobile liquid, and completely miscible with ether. Propylene glycol is very viscous, and is insoluble in ether.

α-Butylene Glycol Diacetate.

0.1 Gram of sodium was dissolved in 25 c.c. of absolute alcohol, and the solution boiled on a steam-bath with 8.7 grams of α-butylene glycol diacetate for eight hours. On distillation, a product (5 grams) was obtained, boiling at 198°, which was insoluble in water and completely soluble in ether. It was concluded to be the unchanged diacetate. An experiment on a larger scale, using one molecular proportion of sodium ethoxide, gave 60 per cent. of the theoretical amount of α-butylene glycol.

ψ-Butylene Glycol Diacetate.

0.1 Gram of sodium was dissolved in 25 c.c. of absolute alcohol, and the solution boiled with 8.7 grams of ψ-butylene glycol diacetate for eight hours. The product consisted of unchanged diacetate, boiling at 188—190°. It was soluble in ether and insoluble in water.

The general method of preparing glycols mentioned on p. 2296 was carried out as follows. 1.15 Grams of sodium were dissolved in 25 c.c. of absolute alcohol containing about 1 per cent. of water, the ester was added, and the mixture was heated for about an hour on a steam-bath in a reflux apparatus. The supernatant liquid was evaporated, and the residue was boiled for about fifteen minutes with 2.3 c.c. of water, and then saturated with carbon dioxide to remove any excess of alkali. The mass was then distilled, and the distillate fractionated. The yield varied from 60 to 85 per cent. of the theoretical.

Ethylene glycol diacetate gave 85 per cent.			
Propylene	"	76	"
Trimethylene	"	63	"
α-Butylene	"	60	"

On classifying the diacetates investigated, it will be seen that they fall into two distinct classes, according to their behaviour with alcoholic sodium ethoxide: (1) those which are hydrolysed by this means, namely, ethylene glycol diacetate, trimethylene glycol diacetate, and α -butylene glycol diacetate; and (2) those which are not hydrolysed, namely, ψ -butylene glycol diacetate and propylene glycol diacetate. It will be noticed that class 2 (except the first) have their acetoxyl groups attached to adjacent carbon atoms, whilst class 1 have them attached to carbon atoms which are not adjacent.

In conclusion, the author desires to acknowledge his indebtedness to the Research Fund Committee of the Chemical Society for a grant which has partly covered the expenses of this research, and also to thank Prof. A. Lapworth and Mr. E. Hope for their advice and encouragement.

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Organic Chemistry.

Observations on the Acetylene Dichlorides. G. CHAVANNE (*Bull. Soc. chim. Belg.*, 1914, 28, 234—240).—The formulae assigned to the isomeric acetylene dichlorides [*s*-dichloroethylenes] in a previous paper (*A.*, 1912, i, 330) on the basis of the rate at which they react with alcoholic potassium hydroxide, are found to require transposition. The isomeride boiling at 60.25° is the *cis*-form, whilst the more reactive isomeride boiling at 48.35° is the *trans*-form. The equilibrium mixture contains 80% of the former and 20% of the latter.

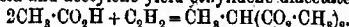
If the *s*-dichlorodibromoothane, which is obtained from either of the isomerides on the addition of bromine, is acted on by zinc in presence of alcohol, the bromine is removed and an equilibrium mixture of the two acetylene dichlorides is obtained. If the dichlorodibromoothane is added slowly to the mixture of zinc and alcohol, the equilibrium mixture is obtained in almost theoretical yield. An explanation of the formation of the two isomerides in this ratio has not yet been found.

Experiments have also been made to determine the rate of addition of bromine by the two isomeric forms. Small quantities of bromine were dissolved in the pure liquids, and the rate of disappearance of the bromine on exposure to the light from a Nernst lamp was measured at about 12°. The reaction proceeds in accordance with the equation for a unimolecular change, although the coefficient increases somewhat during the initial stages of the reaction. The results show that the reaction velocity is about twice as great for the *trans*-form as for the *cis*-form of the dichloride. Experiments with the equilibrium mixture gave an intermediate value for the velocity coefficient. H. M. D.

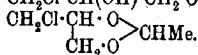
The Presence of an Alcohol and an Acid, each having C_{32} , in the Wax from *Tachardia lacca*. ALBERT GASCARD (*Compt. rend.*, 1914, 159, 258—260).—Lac gum on extraction with boiling alcohol loses all its resin and the greater part of its wax. The residue consists of fragments of wood and insect remains, and on extraction with boiling benzene yields a further small amount of wax, which on purification is shown to be an ester, m. p. 91°. This on saponification with boiling potassium hydroxide yields an alcohol and an acid, the latter being separated by means of its calcium salt. The alcohol crystallises in lozenge-shaped plates, m. p. 88°, and is shown to be dotriacontanol (*lacceryl*), $C_{32}H_{65}\cdot OH$. It yields the corresponding dotriacontanyl iodide, $C_{32}H_{65}I$, m. p. 71°, and on reduction dotriacontane, m. p. 70.5°. The acid obtained by the saponification is dotriacontanoic (*lacceroic*) acid, m. p. 95—96°, giving an ethyl ester, m. p. 76°, which on reduction yields dotriacontanol. W. G.

Preparation of Esters and Ethers of Ethylidene Glycol and Vinyl Alcohol. CHEMISCHE FABRIK GRIESHEIM-ELEKTRO (D.R.P. 271381).—In presence of mercuric salts such as the sulphate or phosphate,

compounds containing hydroxyl or carboxyl groups absorb acetylene with great rapidity, the reaction being often facilitated by the addition of small proportions of catalysts such as mineral acids, acid salts, &c. Thus, acetic acid and acetylene yield ethylidene diacetate,



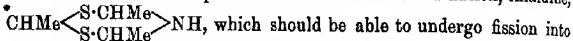
In other instances 1 mol. of the carboxylic or hydroxylic compound reacts with 1 mol. of acetylene; for instance, $\text{CCl}_3\cdot\text{CO}_2\text{H} + \text{C}_2\text{H}_2 = \text{CCl}_3\cdot\text{CO}_2\cdot\text{CH}:\text{CH}_2$ and $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH} + \text{C}_2\text{H}_2 =$



T. H. P.

Phytochemical Formation of Ethyl Mercaptan. C. NEUBERG and F. F. NORD (*Ber.*, 1914, 47, 2264—2271).—It is suggested that the thiocarbimides and organic sulphides found in plants have their origin in the mercaptans. The last-named substances are not easily formed from the corresponding alcohols, but as the latter are possibly produced through the aldehydes in fermentation processes, the possibility of the aldehydes as an important stage in the formation of mercaptans has been considered. The accompanying experimental evidence is in favour of this view.

As the unstable unimolecular thioaldehydes and the very sparingly soluble trimolecular compounds were unsuited to examination, thialdine,



ethyl mercaptan and aldehyde-ammonia, was used. If an alcoholic solution of this substance is added to a solution of sucrose which is in a state of fermentation, the odour of mercaptan is soon evident. The mercaptan was separated from the accompanying carbon dioxide by bubbling the evolved gas through a series of flasks containing a solution of mercuric cyanide; by treating the precipitate of mercuric mercaptide with hydrochloric acid and warming, the mercaptan was obtained in a purer condition and was immediately converted into the lead salt in which form its identity was established. From 20 grams of thialdine, 1.3 of the lead salt was finally obtained.

Only living yeast is able to reduce thialdine in this way in the presence of sugar, and the process presumably is analogous to the production of alcohol from an aldehyde.

D. F. T.

Preparation of Acetic Anhydride. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 273101).—The preparation of acetic anhydride by passing chlorine into a mixture of an acetate with sulphur necessitates the use of very low temperatures obtainable only with the help of a refrigerating machine. This disadvantage is obviated by replacing the sulphur by sulphur mono- or di-chloride or a mixture of the two, the reactions, which take place at about 20% and give good yields of the anhydride, being represented by the equations: $16\text{CH}_3\cdot\text{CO}_2\text{Na} + \text{S}_2\text{Cl}_2 + 5\text{Cl}_2 = 12\text{NaCl} + 2\text{Na}_2\text{SO}_4 + 8\text{Ac}_2\text{O}$ and $8\text{CH}_3\cdot\text{CO}_2\text{Na} + \text{SOCl}_2 + 2\text{Cl}_2 = 6\text{NaCl} + \text{Na}_2\text{SO}_4 + 4\text{Ac}_2\text{O}$.

T. H. P.

Preparation of Cellulose Esters of Fatty Acids. CHEMISCHE FABRIK VON HEYDEN A.-G. (D.R.-P. 273029).—Aliphatic esters of cellu-

lose or its transformation products are obtained by treatment of the dried cellulosic material with anhydrides of fatty acids in presence of chlorides of sulphuric acid without heating or at the ordinary temperature.

T. H. P.

Phosphates of $\alpha\beta$ -Distearin. R. R. RENSCHAW and R. R. STEVENS (*J. Amer. Chem. Soc.*, 1914, 36, 1770—1772).—Grün and Kade (A., 1913, i, 158) have described certain distearin phosphates obtained by the action of phosphoric oxide on distearin. Similar experiments have been carried out by the authors, who have confirmed the work on the primary orthophosphate, and have isolated a sodium salt of stearin pyrophosphate, $C_{17}H_{35}\cdot CO\cdot O\cdot CH_2\cdot CH\cdot O\cdot PO_2Na$;
 $CH_2\cdot O\cdot PO_2Na \rightarrow O$;
 the corresponding silver, barium, and calcium salts were prepared.

E. G.

Catalytic Reduction of Oleic Acid and Cottonseed Oil by means of Hydrogen in Presence of Finely Divided Nickel. T. W. A. SHAW (*J. Soc. Chem. Ind.*, 1914, 33, 771—774).—The first series of experiments deals with the reduction of oleic acid vapour. An apparatus is described in which the vapour of oleic acid is carried by a current of purified hydrogen under diminished pressure into a cylinder, heated at about 300°, containing broken pumice impregnated with about 13—14% of nickel (reduced from the oxide by hydrogen at about 300°). The extent of the reduction is determined by estimating the iodine number of the product by the Wys-Hübl method. Under 100, 150, and 200 mm. pressure, 5, 15, and 20% respectively of the oleic acid vapour is reduced; these values are practically unchanged when the products are again passed through the apparatus.

The results indicate a state of equilibrium in the gaseous phase between hydrogen, oleic acid, and stearic acid; however, when stearic acid vapour and hydrogen are passed through the apparatus, the iodine number of the product is zero.

In a second series of experiments in the same apparatus, liquid oleic acid is kept in contact with the catalyst at about 275° for different periods of time, the pressure of the hydrogen being maintained at 1 atmos.; about 45% of the acid is reduced after nine hours.

A third series of experiments deals with the reduction of liquid oleic acid under very great pressures. An apparatus is described in which oleic acid is sprayed, by means of a specially designed feed-valve and glass sprinkler (not a soldered brass rose, because the acid dissolves from this some constituent which poisons the catalyst), over the catalyst in an atmosphere of hydrogen at a definite temperature and pressure, the rate of flow being about 40 c.c. per hour. At a temperature of 250°, the amount of oleic acid reduced is 4, 20, and 35% under pressures 5, 25, and 50 atmos. respectively.

A few experiments performed with cottonseed oil show that at 200°, and under pressures of 25 and 50 atmos., more than 50% of the glyceride is reduced and a hard product, m. p. about 50°, is obtained.

C. S.

Preparation of Glycerol Halogenhydrins and Esters of Polyhydroxyaliphatic Acids. ADOLF GRÜN (D.R.-P. 272337).—When castor oil or oxidised linseed oil, etc., is treated directly or in solution under pressure with the calculated proportion or an excess of hydrogen haloid, either as gas or dissolved in alcohol, the principal reactions taking place are as follows: (1) the triglyceride is converted by the hydrogen haloid into ricinoleic acid and its chlorohydrin ester, the latter then undergoing decomposition into chlorohydrin and free acid; (2) $20\text{H}\cdot\text{C}_{17}\text{H}_{33}\cdot\text{CO}_2\text{H} - \text{H}_2\text{O} = \text{OH}\cdot\text{C}_{17}\text{H}_{32}\cdot\text{CO}\cdot\text{O}\cdot\text{C}_{17}\text{H}_{32}\cdot\text{CO}_2\text{H}$ and $30\text{H}\cdot\text{C}_{17}\text{H}_{32}\cdot\text{CO}_2\text{H} - 2\text{H}_2\text{O} =$

$\text{OH}\cdot\text{C}_{17}\text{H}_{32}\cdot\text{CO}\cdot\text{O}\cdot\text{C}_{17}\text{H}_{32}\cdot\text{CO}\cdot\text{O}\cdot\text{C}_{17}\text{H}_{32}\cdot\text{CO}_2\text{H}$;
(3) the di- and tri-ricinoleic acids undergo esterification by the alcohol present. The principal constituents of the resultant product are the mono- and di-chlorohydrins of glycerol and esters of polyricinoleic acids, but small proportions of glycerol and free di- and tri-ricinoleic acids are also present.

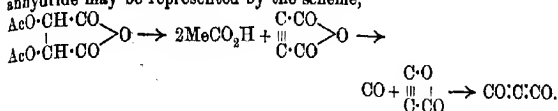
T. H. P.

Optical Decomposition of the Iridotrioxalates. M. DELÉPINE (*Compt. rend.*, 1914, 159, 239–241).—The author has prepared optically active iridotrioxalates of the type $\text{M}_3\text{Ir}(\text{C}_2\text{O}_4)_3$, by preparing the strychnine salts from the racemic potassium salt, and separating these into the dextro- and laevo-components by fractional precipitation. The potassium salt was prepared by the action of a solution of potassium oxalate on potassium iridi- or irido-chlorides or potassium iridodichloridoxalate in an autoclave at 130° for eight hours. This salt after crystallisation was fractionally precipitated by strychnine sulphate, giving the two crystalline strychnine salts, differently hydrated, which in the anhydrous state, $(\text{C}_{21}\text{H}_{22}\text{N}_8\text{O}_2)_3$, $\text{H}_3\text{Ir}(\text{C}_2\text{O}_4)_3$, had $[\alpha]_D + 11.6^\circ$ and -56.4° respectively. These on decomposition with potassium hydroxide in aqueous solution gave the *d*- and *l*-potassium salts, $\text{K}_3\text{Ir}(\text{C}_2\text{O}_4)_3 \cdot 2\text{H}_2\text{O}$, $[\alpha]_D \pm 82^\circ$, and with barium hydroxide the *d*- and *l*-barium salts, $\text{Ba}_3[\text{Ir}(\text{C}_2\text{O}_4)_3] \cdot 15\text{H}_2\text{O}$, $[\alpha]_D \pm 62.5^\circ$. The silver salts prepared from these active salts by double decomposition could only be obtained in the form of amorphous, granular masses. The active salts in solution at 100° show a slow diminution of a few hundredths of a degree per hour in their optical activity. The *d*-potassium iridotrioxalate shows an anomalous rotatory dispersion and a circular dichroism. The maximum rotation is in the blue portion of the spectrum, and it disappears in the violet.

W. G.

Pyrogenic Formation of Carbon Suboxide from γ -Lactones. ERWIN OTT (*Ber.*, 1914, 47, 2388–2393).—When diacetyl tartaric anhydride and acetoxymaleic anhydride are heated, they readily suffer decomposition into acetic acid and carbon suboxide. It is assumed that acetylenedicarboxylic anhydride is an intermediate product, for an appreciable quantity of carbon suboxide is only obtained from these acetylated 1:2-dicarboxylic anhydrides that, by losing acetic acid, can produce the acetylenic anhydride. Diacetoxymaleic anhydride, for example, yields acetic acid and keten, and only about 2% of carbon suboxide. Keten is also a product of the decomposition of triacetin, but not of all acetyl derivatives. The one feature common to these

compounds is the tendency to the elimination of acetic acid. The decomposition of acetylenedicarboxylic anhydride is accompanied by the production of carbon monoxide, which is often formed when 1:2-dicarboxylic acid derivatives, ethyl oxalate, for example, are heated. Assuming that the carbon suboxide is first set free in the form of β -oxypropiolactone, the decomposition of diacetyltartaric anhydride may be represented by the scheme,



Diacetyltartaric anhydride may be obtained in quantitative yield from acetic anhydride, tartaric acid and sulphuric acid (Wohl and Osterlin, A., 1901, i, 365), and is a very suitable material for the preparation of carbon suboxide. For this purpose, it is quickly distilled under reduced pressure from a long-necked flask in a bath at 180—185°, over a glowing platinum spiral which is so adjusted that decomposition of the vapours is complete. In order to estimate the yields, the flask was connected with a receiver cooled to -80°, and a vessel containing aniline. The amount of acetic acid condensed represented a yield of 87%, and the malonanilide which collected in the second receiver corresponded with a 42.5% yield of carbon suboxide.

Acetoxymaleic anhydride (*ibid.*) sublimes in a vacuum at 65° and forms compact crusts, m. p. 91°. It decomposed at 140—150° and gave a 73% yield of acetic acid, 37% of malonanilide, 69.4% of carbon monoxide, and 31% of carbon dioxide. Diacetoxymaleic anhydride (Fenton, T., 1896, 69, 551) decomposed at 160—170°, and gave acetic acid 73%, carbon suboxide 2%, keten, weighed as acetanilide, 10%, carbon monoxide 91.5%, and carbon dioxide 70%. Triacetin was similarly treated at 155°, and gave acetic acid, acraldehyde and keten (26%). J. C. W.

Preparation of Cupric Cholate. KNOLL & Co. (D.R.-P. 273317).—The interaction of solutions of a cupric salt and of sodium cholate in presence of methyl or ethyl alcohol yield *cupric cholate*, $\text{Cu}(\text{C}_{24}\text{H}_{49}\text{O}_5)_2$, which exerts a bactericidal action; it dissolves in 100 parts of castor oil. T. H. P.

Tetra-acetylmucyl Chloride and Azoimide. Decomposition of the Latter by Heat. OTTO DIELS and FRITZ LÖFLUND (*Ber.*, 1914, 47, 2351—2355).—The authors have attempted the ring condensation of tetra-acetylmucic acid derivatives, but without success. The elimination of chlorine from the acid chloride was without result, and the action of heat on the azoimide seemed to follow an unusual course, for the nitrogen compound which was obtained was very stable.

Tetra-acetylmucic acid was shaken with phosphorus pentachloride and acetyl chloride for an hour or so, when the *chloride*, $\text{C}_{14}\text{H}_{16}\text{O}_{10}\text{Cl}_2$, separated quantitatively in small, silky needles, m. p. 179—180° (compare Jacoby, *Diss.*, Berlin, 1907). The *hydrazide*, $\text{C}_{14}\text{H}_{22}\text{O}_{10}\text{N}_4$, was prepared by adding the powdered chloride in small quantities to a 50%

solution of hydrazine hydrate, with vigorous stirring, and formed a very sparingly soluble, white powder. This was converted into *tetraacetylmucylazoimide*, $C_{14}H_{16}O_{10}N_6$, by the action of nitrous fumes. The bistriazo-compound was also prepared by mixing an acetone solution of the chloride with a solution of sodium azoimide in dilute acetone. It forms long prisms which decompose at above 108° , then re-solidify, and melt again at 139° . It was gradually heated to 110° in ethyl malonate, whereby two molecular proportions of nitrogen were evolved and a clear solution remained, from which, on cooling, the compound, $C_{14}H_{16}O_{10}N_2$, separated in large prisms, m. p. 139° .

J. C. W.

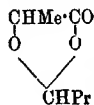
Oxalocitrolactone and its Transformation into Tricarballic Acid. H. GAULT (*Compt. rend.*, 1914, 159, 256—258. Compare this vol., i, 384, 484).—Oxalocitrolactone on heating with water or hydrochloric acid in sealed tubes at 180° , yields tricarballic acid and a large amount of resinous substances. On heating with alcohol in an autoclave at 180 – 200° , it yields ethyl oxalate (3%), ethyl tricarballylate (30%), and ethyl propanetetra-carboxylate (60%). The two latter esters on hydrolysis with acid give a quantitative yield of tricarballic acid. Under the influence of hydrolysing agents the ketolactonic ring of oxalocitrolactone is opened or not, according as the hydrolysis is effected at a high (180 – 200°) or a medium temperature (100 – 120°).

W. G.

Preparation of Acraldehyde. EDGAR J. WITZEMANN (*J. Amer. Chem. Soc.*, 1914, 36, 1766—1770).—Wohl and Mylo (A., 1912, i, 677) have described a method for preparing acraldehyde from glycerol in which anhydrous magnesium sulphate is used as catalyst. This method is very satisfactory, but involves the use of special expensive apparatus. A modification is now described in which the apparatus is so simplified as to be capable of construction from ordinary stock materials. The modified method does not give quite such large yields of pure acraldehyde as were obtained by Wohl and Mylo, but it is much more readily available for ordinary use.

E. G.

Syntheses by means of Organometallic Derivatives of Zinc: Aldehydes. E. E. BLATSE (*Bull. Soc. chim.*, 1914, [iv], 15, 661—666).—Lactic acid and α -hydroxyisobutyric acid when warmed with an excess of a mixture of formic acid and acetic anhydride yield the corresponding formic esters, which, like their acid chlorides, condense with zinc propyl iodide to give methylpropyl- and dimethylpropyl-cycloacetals, which on hydrolysis give butaldehyde. Lactic acid gives α -formoxypropionic acid, $CHO \cdot O \cdot CHMe \cdot CO_2H$, m. p. 78° , b. p. 120 – $121^\circ/13$ mm., which yields an acid chloride, b. p. $59^\circ/19$ mm., and an amide, long needles, m. p. 182° . The acid chloride condenses with zinc propyl iodide to give 1-methyl-4-propylcycloacetal (annexed formula), b. p. $82^\circ/17$ mm.



α -Hydroxyisobutyric acid yields α -formoxyisobutyric acid, $CHO \cdot O \cdot CMe_2 \cdot CO_2H$, needles, m. p. 64 – 65° , b. p. 125 – $126^\circ/15$ mm., giving an acid chloride, a dense liquid with a very disagreeable odour, b. p. 53 – $54^\circ/14$ mm.,

and an *anilide*, prismatic needles, m. p. 100—101°. The acid chloride with zinc propyl iodide yields 1:1-*dimethyl-4-propylcycloacetal* (annexed formula), b. p. 84°/20 mm.

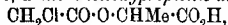
Both these *cycloacetals* are readily hydrolysed on boiling with aqueous oxalic acid, giving butaldehyde, b. p. 73—74°, and the original hydroxy-acid. Both of the formoxy-acids are rapidly saponified on exposure to air.

W. G.

Syntheses by means of Mixed Organometallic Derivatives of Zinc. α -Monochloroketones. E. E. BLAISE (*Bull. Soc. chim.* 1914, [iv], 15, 666—673. Compare preceding abstract).—By the following series of reactions the author has prepared a number of α -chloro-ketones. An α -chloro-acid chloride was condensed with a suitable α -hydroxy-acid, either lactic acid or α -hydroxyisobutyric acid, and the resulting ester acid converted into its acid chloride. This acid chloride was then treated with the necessary zinc alkyl iodide, giving a chloro-*cycloacetal*, which on hydrolysis gave the required α -chloro-ketone.

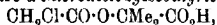
The required α -chloro-acid chlorides were prepared by chlorinating the corresponding alkylmalonic acids in solution in carbon tetrachloride by a current of dry chlorine, decomposing the chloroalkylmalonic acid by heat and treating the resulting α -chloro-acid with thionyl chloride. Thus ethylmalonic acid yields *α -chloroethylmalonic acid*, needles, m. p. 106—107°, which is decomposed on heating at 140°, yielding *α -chlorobutyric acid*, b. p. 109.5°/24 mm., giving the corresponding *acid chloride*, b. p. 62—63°/70 mm. and 51—52°/41 mm.

On condensing lactic acid with α -chlorobutyryl chloride in the presence of diethylaniline, *α -chloroacetoxypropionic acid*,



is obtained, m. p. 76°, b. p. 160—162°/15 mm., giving an *acid chloride*, b. p. 94°/11 mm., and an *anilide*, white needles, m. p. 95—96°.

Similarly prepared are *α -chloroacetoxyisobutyric acid*,



m. p. 75°, its *acid chloride*, a viscous liquid, b. p. 97°/12 mm., and its *anilide*, long needles, m. p. 127.5°; *α -chlorobutyroxyisobutyric acid*, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{O}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$, slender needles, m. p. 61—62°, its *acid chloride*, b. p. 106°/11 mm., and its *anilide*, m. p. 65—66°.

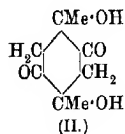
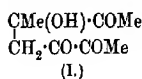
α -Chloroacetoxypropionyl chloride gives with zinc ethyl iodide the *cycloacetal*, $\begin{array}{c} \text{CHMe}\cdot\text{O} \\ \diagup \quad \diagdown \\ \text{CO} \quad \text{O} \end{array} \text{CET}\cdot\text{CH}_2\text{Cl}$, b. p. 106°/12 mm., which on hydrolysis yielded chloromethyl ethyl ketone, b. p. 67—68°.

α -Chloroacetoxyisobutyryl chloride yields with zinc propyl iodide the *cycloacetal*, $\begin{array}{c} \text{CMe}_2\cdot\text{O} \\ \diagup \quad \diagdown \\ \text{CO} \quad \text{O} \end{array} \text{CPr}\cdot\text{CH}_2\text{Cl}$, b. p. 110.5°/10 mm., which gives *chloromethyl propyl ketone*, b. p. 154—156°/760 mm. or 58—59°/17 mm., yielding a *semicarbazone*, m. p. 157°. Together with the above *cyclo-*

acetal a second *cycloacetal*, $\begin{array}{c} \text{CMe}_2\cdot\text{O} \\ \diagup \quad \diagdown \\ \text{CO} \quad \text{O} \end{array} \text{CH}\cdot\text{CH}_2\text{Cl}$, b. p. 91.5°/11 mm., is obtained, which on hydrolysis yields chloroacetaldehyde.

α -Chlorobutyroxyisobutyryl chloride yields with zinc ethyl iodide the cycloacetal, $\begin{array}{c} \text{CMe}_2\text{O} \\ \text{CO}-\text{O} \end{array} \text{CET} \cdot \text{CHClEt}$, b. p. 118.5°/12 mm., which on hydrolysis gives ethyl α -chloro-*n*-propyl ketone, b. p. 53.5°/17 mm. W. G.

Properties, Structure, and Derivatives of the Dimeric Diacetyl. OTTO DIELS, W. M. BLANCHARD, and H. VON DER HEYDEN (*Ber.*, 1914, 47, 2355—2365).—As an intermediate product in the condensation of diacetyl, Pechmann isolated a colourless oil which was found to be a dimeride of diacetyl, and to yield a trihydrazone. On



account of the latter fact, Pechmann and Wedekind (*A.*, 1895, i, 647) decided in favour of the formula I. It would be strange for an unsymmetrical product to arise from diacetyl by simple means, and such a compound as the above (formula I) should be unstable and intensely coloured. The authors now bring forward evidence in favour of Pechmann's alternative formula II.

In the first place, they find that the compound may be obtained as a colourless solid, but that it develops a yellow colour on melting or distilling, and in many solvents. It seems probable, therefore, that, although the colourless compound can scarcely contain adjacent carbonyl groups, it can readily pass into such a state. The formation of a triphenylhydrazone, a quinoxaline and disemicarbazone, does not really help to decide on the true formula, but it is hoped that two oxygen-free compounds, obtained by the action of hydrazine under different conditions, may throw some light on the question. Many fruitless attempts were also made to determine the presence and number of hydroxyl groups in the aldol, but it was at last discovered that carbethoxycarbimide (*A.*, 1906, i, 237; 1908, i, 613) forms a mono- and a di-derivative. This agrees with the cyclic formula, which is further supported by refractometric evidence, and more readily explains the formation of *p*-xyloquinone by the action of 33% potassium hydroxide on the aldol.

For the preparation of the dimeric diacetyl, *N*-potassium hydroxide was allowed to drop into an ice-cold, aqueous solution of the diketone, when the brilliant yellow colour faded. The product was faintly acidified and submitted to prolonged extraction with ether. The residue from the dried extract was then heated at 80° under reduced pressure to remove diacetyl, and finally distilled in a high vacuum, a fraction with b. p. 95—102°/0.2 mm. being collected. This was left over phosphoric oxide in the cold, when, especially after inoculation, it solidified to a hard mass which was freed from traces of oil by hydraulic pressure. After crystallisation from a mixture of ether and light petroleum, it was obtained in large, well-developed, glistening, colourless, hard crystals. The m. p. varied from 44—46° for slow heating to about 58° for quick heating. The refraction of the super-cooled substance was measured for the red hydrogen line at 29.8°,

D_4^{20} being 1.15597, and the observed molecular refraction, 40.20, agreed with the theoretical value, 39.94, based on Clarke's figure, 27.78, for cyclohexanedione (T., 1912, 101, 1804).

The *monocarbethoxycarbimide* derivative, $C_{12}H_{17}O_7N$, gradually separates when cold, ethereal solutions of the components are mixed. It forms white, velvety needles, m. p. 109°. When the undiluted reagents are mixed, much heat is developed, and a mixture of mono- and di-derivatives is formed. On cooling the ethereal solution, the mono-derivative separates, leaving the *dicarbethoxycarbimide* compound in the mother liquor. The latter forms coarse, fibrous crystals, m. p. 150°.

When an aqueous solution of the aldol is mixed with a solution of hydrazine hydrate in the cold and the water is subsequently distilled under reduced pressure, a syrup is formed, which deposits from methyl alcohol the colourless *hydrazone*, $C_8H_{12}N_4$, in stout crystals, m. p. 161—163°. By adding hydrazine hydrate, drop by drop, to the pure aldol, however, a yellow liquid is obtained which solidifies when acidified by 50% acetic acid and cooled in ice. This *hydrazone*, $C_{16}H_{20}N_6$, forms brilliant golden-yellow prisms, m. p. 185°, which crystallise in an almost colourless form from very dilute alcohol, but recrystallise from pure alcohol with the original colour. A mixture of the colourless hydrazone with potassium hydroxide and platinised alumina was heated until reaction set in and then distilled, when the *base*, $C_8H_{12}N_4$, was collected as a yellow oil, b. p. 220—230°, 132°/11 mm.; it formed a *methiodide*, $C_9H_{15}N_2I$, in large, yellow crystals, m. p. 152°.

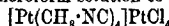
The *disemicarbazone* of the aldol, $C_{16}H_{18}O_4N_6$, was obtained by mixing concentrated aqueous solutions of the aldol and the hydrochloride, in colourless, slender needles, m. p. 225° (decomp.). Similarly, on mixing aqueous solutions of the aldol and *o*-phenylenediamine, the *quinoxaline* (†), $C_{14}H_{16}O_2N_2$, separated in glistening, yellow needles, m. p. 112—113°. The *semicarbazone* of the latter, $C_{15}H_{18}O_2N_2$, forms well-developed, almost colourless plates, m. p. 185°. J. C. W.

Problems of Celluloid Chemistry and the Necessity of Colloido-Chemical Views in the Industry. H. SCHWARZ (*Koll. Chem. Beilhefte*, 1914, 6, 90—126).—The possible application of the theories associated with the chemistry of colloids to the problems of the celluloid industry is discussed with special reference to the factors which influence the stability of the substance. In particular, the author deals with the relationship between the stability of celluloid and the stability of the nitrocellulose employed in its production. As a means of determining the presence of small quantities of unstable substances in nitro-cellulose, the "heat-test" is adversely criticised.

The fact that traces of free acid are responsible for the instability of celluloid would seem to be well established, and the methods employed in practice for the neutralisation of the free acid are discussed. It is shown that colloidal ant-acids are particularly efficient in this connexion, and that the activity of these increases with the quantity present. Celluloid itself is regarded as a colloidal mixture of nitrocellulose and camphor.

H. M. D.

Preparation of Complex Compounds of Bivalent Platinum. L. TSCHUGAEV (*Compt. rend.*, 1914, 159, 188—189).—By the use of tripropylamine platinochloride, obtained by the double decomposition of tripropylamine hydrochloride and ammonium platinochloride, the author has been able to use organic solvents for the preparation of complex platinum compounds. Thus, this platinochloride reacts with methylcarbylamine in chloroform solution to give the compound,



(compare Tschugaev and Teearu, this vol., i, 392). With hydrazine in the same solvent, it yields the compound, $[\text{Pt}(\text{N}_2\text{H}_4)_4]\text{Cl}_2$. Tripropylamine platinochloride can also be used for the preparation of platinochlorides from aromatic phosphines, arsines and stibines, which are quite insoluble in water.

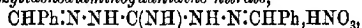
W. G.

Preparation of a Stable, Solid Compound of Hydrogen Peroxide and Hexamethylenetetramine. DIAMALT ARTIEN-GESELLSCHAFT (Austrian Patent 63538).—This compound, which is obtained by dissolving hexamethylenetetramine, with cooling, in hydrogen peroxide solution and precipitation by means of an organic solvent, is moderately stable and possesses antiseptic properties. Its stability is enhanced by the addition of: (1) an anhydride, such as that of lactic or glycolic acid or the acetyl derivative of an aromatic hydroxy-acid, which absorbs the ammonia formed on decomposition, and (2) a protein or polysaccharide, which absorbs the formaldehyde also formed.

T. H. P.

Preparation of Aminoguanidine and of Diaminoguanidine. GUIDO PELLIZZARI and AUGUSTO GAITER (*Gazzetta*, 1914, 44, ii, 72—77).—The authors have established the conditions under which aminoguanidine hydrogen carbonate (compare Thiele, A., 1899, i, 7) can be obtained simply and in almost theoretical yield from calcium cyanamide, hydrazine sulphate and potassium carbonate. *Aminoguanidine hydrobromide*, $\text{CH}_6\text{N}_4\cdot\text{HBr}$, forms colourless, prismatic needles, m. p. 149° (decomp.).

Now that hydrazine hydrate is obtainable of 100% purity, the authors have modified the conditions for the preparation of diaminoguanidine hydrobromide by the action of cyanogen bromide (compare Pellizzari and Cantoni, A., 1905, i, 576). *Diaminoguanidine nitrate*, $\text{CH}_7\text{N}_5\cdot\text{HNO}_3$, forms groups of colourless, prismatic needles, m. p. 143°. *Dibenzylidenediaminoguanidine nitrate*,



forms white needles, m. p. 211—212°, turning an intense red in the light.

T. H. P.

Triaminoguanidine. GUIDO PELLIZZARI and AUGUSTO GAITER (*Gazzetta*, 1914, 44, ii, 78—85).—The formation of triaminoguanidine hydrochloride by boiling hydrazine hydrate with excess of carbon tetrachloride in a current of ammonia for some days gives a small yield of a preparation difficult to purify (compare Stollé, A., 1904, i, 980). The authors find that triaminoguanidine salts may be obtained readily by heating concentrated alcoholic or aqueous solutions of the salts of either guanidine or its amino- or its diamino-derivative

with the calculated proportion of hydrazine hydrate for two to five hours. Salts of triaminoguanidine react easily with aldehydes, giving salts of the condensation products of the triaminoguanidine with 3 mols. of the aldehydes.

Triaminoguanidins nitrate, $\text{NH}_2\cdot\text{N}:\text{C}(\text{NH}\cdot\text{NH}_2)_2\cdot\text{HNO}_3$, forms colourless needles, m. p. 216° (decomp.).

Tribenzylidenetriaminoguanidine nitrate,
 $\text{CHPh}\cdot\text{N}:\text{N}:\text{C}(\cdot\text{NH}\cdot\text{N}:\text{CHPh})_2\cdot\text{HNO}_3\cdot 3\text{H}_2\text{O}$,
 forms slender, yellowish-white needles.

Triaminoguanidine hydrobromide, $\text{CH}_3\text{N}_6\cdot\text{HBr}$, forms colourless, shining needles, m. p. 232° (decomp.), or somewhat lower if the heating is slow.

Tribenzylidenetriaminoguanidine hydrobromide, $\text{C}_{22}\text{H}_{20}\text{N}_6\cdot\text{HBr}\cdot 3\text{H}_2\text{O}$, forms shining, yellow crystals, and has no definite melting point, but decomposes at about $145\text{--}150^\circ$.

Triaminoguanidine hydrochloride has m. p. 231° (decomp.); Stollé (*loc. cit.*) found 229° . Its tribenzylidene derivative crystallises with $3\text{H}_2\text{O}$, and the crystals effloresce and lose hydrogen chloride in the air.

Tribenzylidenetriaminoguanidine forms small, yellow needles m. p. 198° ; Stollé (*loc. cit.*) gave 196° .

Triaminoguanidine thiocyanate, $\text{CH}_3\text{N}_6\cdot\text{HCNS}$, forms slender, shining needles, m. p. 136° , and the *picrate*, $\text{CH}_3\text{N}_6\cdot\text{C}_6\text{H}_3\text{O}_2\cdot\text{N}_3$, long, yellow needles or shining lamellar crystals, m. p. 171° .

Triaminoguanidine sulphate and oxalate are difficult to purify owing to their extremely high solubility in water. T. H. P.

Action of Chloroacetic Acid on Semicarbazide and Hydrazine. J. R. BAILEY and W. T. READ (*J. Amer. Chem. Soc.*, 1914, **36**, 1747—1766).—The action of chloroacetic acid on hydrazine and phenylhydrazine has already been studied, but its action on semicarbazide has not hitherto been investigated. The present work was therefore undertaken.

When potassium chloroacetate and semicarbazide are heated together in aqueous solution, semicarbazinodiacetic acid is produced, together with a small quantity of semicarbazinoacetic acid. On evaporating the product of the reaction to dryness and treating the residue with alcohol and hydrochloric acid, the ester of semicarbazinodiacetic acid is obtained. *Methyl semicarbazinodiacetate*,

$\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}(\text{CH}_2\cdot\text{CO}_2\text{Me})_2$,
 m. p. $143\text{--}5^\circ$, crystallises in long needles; the corresponding *ethyl ester*,
 m. p. 91° , forms thin plates. By the action of hydrazine hydrate (2 mols.) on the methyl ester (1 mol.), *semicarbazinodiacetohydrazide*,

$\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}(\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2)_2$,
 m. p. 149° , is produced, which yields a *dibenzylidene* compound,

$\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}(\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}:\text{CHPh})_2$,
 m. p. 178° (decomp.). Methyl semicarbazinodiacetate is decomposed by nitrous acid with formation of methyl iminodiacetate (Jongkees, A., 1908, i, 959).

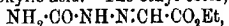
If ethyl or methyl semicarbazinodiacetate is treated with an alcoholic solution of sodium ethoxide, *ethyl 3:5-dihydroxy-1:6-dihydro-1:2:4-*

triazine-1-acetate, $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{N}<\text{N}=\text{C}(\text{OH})\text{CH}_2\cdot\text{C}(\text{OH})\text{N}>\text{N}$, m. p. 138.5° , is produced which crystallises in slender needles; the corresponding methyl ester, m. p. 183.5° , forms short, stout prisms.

Semicarbazinodiacetic acid crystallises in long, rectangular plates and decomposes at 161° ; its calcium, barium, and zinc salts are described.

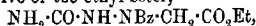
When methyl semicarbazinodiacetate is heated with potassium hydroxide, hydrazinodiacetic acid is produced. A modification of Curtius and Hussong's method (A., 1911, i, 401) of preparing this acid is described which gives a greatly increased yield. Hydrazinodiacetic acid becomes yellow at 165° and decomposes at 176° ; its solubility in water is 1:108 at 22° and 1:46 at 100° . The barium and zinc salts are described; the methyl ester has m. p. 174.5° (decomp.). By the action of phenylthiocarbimide on methyl hydrazinodiacetate, methyl phenylthiocarbamidoaminodiacetate, $\text{NHPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{N}(\text{CH}_2\cdot\text{CO}_2\text{Me})_2$, m. p. 120° , is obtained, which crystallises in long needles. Formaldehyde reacts with hydrazinodiacetic acid with formation of a pale yellow substance which has not been investigated. When hydrazinodiacetic acid is treated with nitrous acid, iminodiacetic acid is produced. Confirmation was obtained of Curtius and Hussong's observation (*loc. cit.*) that hydrazinodiacetic acid is readily decomposed when heated with mineral acids, half the nitrogen of the molecule being eliminated as ammonia, and glycine and nitrilotriacetic acid were isolated from the reaction products.

Methyl and ethyl semicarbazinodiacetates are readily oxidised with potassium permanganate or bromine with formation of esters of the semicarbazone of glyoxylic acid. The ethyl ester,



melts at 211° (decomp.) when heated slowly, and decomposes at about 218° when heated rapidly; Simon and Chavaune (A., 1907, i, 110) state that it has m. p. 228° (decomp.). The corresponding methyl ester has m. p. 206° (decomp.).

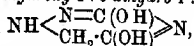
When glyoxylic acid semicarbazone is reduced with sodium amalgam and the product esterified by means of alcoholic hydrochloric acid, ethyl semicarbazinoacetate is produced in yield amounting to 66% of the theoretical; the hydrochloride of this ester decomposes at 170° . Semicarbazinoacetic acid, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, has m. p. 143° . The benzoyl derivative of the ethyl ester,



m. p. 172° , forms rectangular plates, and when heated with 10% potassium hydroxide solution it is converted into 3-hydroxy-5-phenyltriazole-1-acetic acid, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{N}<\text{N}=\text{C}(\text{OH})\text{CPh}\cdot\text{N}>$, m. p. $253-256^\circ$

(decomp.), which furnishes an ethyl ether, m. p. 145° . Phenylthiocarbimide reacts with ethyl semicarbazinoacetate to form 2-thio-1-carbamido-3-phenylhydantoin, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}<\text{CS}-\text{NPh}\text{CH}_2\cdot\text{CO}>$, m. p. 211° (decomp.), which crystallises in thin plates. The nitroso-derivative of ethyl semicarbazinoacetate, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}(\text{NO})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, has m. p.

99–102° (decomp.). By the action of sodium ethoxide on ethyl semicarbazinoacetate, 3:5-dihydroxy-1:6-dihydro-1:2:4-triazine,



m. p. 221°, is produced, which forms prismatic plates.

Ethyl semicarbazinoacetate (Thiele and Bailey, A., 1899, i, 169) can be obtained from pyruvic acid semicarbazone by a method similar to that used for the preparation of ethyl semicarbazinoacetate; its nitroso-derivative has m. p. 134.5° (decomp.). E. G.

Amino-acids. I. A. GEAKE and M. NIERENSTEIN (*Zeitsch. physiol. Chem.*, 1914, 92, 149–153).—The authors find that amino-acids do not undergo methylation when treated, in ethereal suspension, with diazomethane, the amino-acid being recovered unchanged. This is regarded as supporting Willstätter's betaine-structural formula for the amino-acids, for example, $\text{CH}_2 \begin{array}{c} \text{CO} \\ \text{NH}_3 \end{array} \text{O}$ instead of $\text{CH}_2 \begin{array}{c} \text{CO}_2\text{H} \\ \text{NH}_3 \end{array}$.

According to this view, the acetylated amino-acids, possessing a free carboxyl group, might be expected to react with diazomethane, and as a matter of fact, it is found that the methyl ester of carboethoxyglycine is readily formed on treatment of the corresponding acid with diazomethane. H. W. B.

Transformations of *d*-α-Amino-α-methylbutyric Acid. EMIL FISCHER and RICHARD VON GRÄVENITZ (*Annalen*, 1914, 406, 1–11).—The addition of hydrogen cyanide to methyl ethyl ketone proceeds so rapidly after the addition of 2 or 3 drops of very concentrated potassium carbonate that cooling is necessary. *dl*-α-Amino-α-methylbutyric acid, ultimately obtained in 72% yield, forms rhombic, apparently holohedral crystals containing H_2O [α : β =0.81:1]. The acid and boiling 99% formic acid yield the *formyl* derivative, m. p. 175.5–176° (decomp. corr.), which is resolved into its active components by brucine. The *d*-*formyl* derivative, thus obtained in a pure state, resembles the inactive compound in crystalline form and solubility, but decomposes at a slightly higher temperature. By heating with 10% hydrobromic acid on the water-bath and subsequent treatment with lead oxide, it yields *d*-α-amino-α-methylbutyric acid, colourless needles, containing H_2O , which sublimes without melting, has $[\alpha]_D^{25}$ 11.0° in water and $[\alpha]_D^{25}$ 7.26° in 20% hydrochloric acid, and is not appreciably racemised by prolonged boiling with water or 2*N*-sodium hydroxide.

l-α-Amino-α-methylbutyric acid has been obtained by Ehrlich in 1908 by the partial fermentation of the racemic acid by yeast. The authors' method is less convenient than this, but has the advantages that both the active components can be isolated, and the *d*-acid is obtained in a purer form than Ehrlich's *l*-acid.

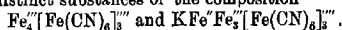
The *d*-acid is converted into optically inactive products by nitrosyl bromide and into *dl*-α-hydroxy-α-methylbutyric acid by nitrous acid; it is useless, therefore, for the study of the Walden inversion.

C. S.

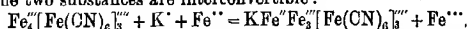
Action of Carbon Dioxide on Calcium Cyanamide. C. MANU-ELLI (*Ann. Chim. Applicata*, 1914, 1, 493–494).—The inefficiency of

calcium cyanamide as a fertiliser and its injurious effect on the labourers who spread it are attributed to the presence of free lime. The author has made investigations to ascertain if these inconveniences are avoidable by replacing the current of nitrogen by one of carbon dioxide during the cooling of the calcium cyanamide and thus converting the free lime into calcium carbonate. It is, however, found that such procedure is accompanied by elimination of a very considerable proportion of the nitrogen of the calcium cyanamide. T. H. P.

Prussian Blue and Turnbull's Blue. IV. ERICH MÜLLER (*J. pr. Chem.*, 1914, [ii], 90, 119—135. Compare A., 1909, i, 142, 705; 1911, i, 844; this vol., i, 504).—From the ratio of ferrous to ferric iron in the precipitates formed by the interaction of potassium ferrocyanide and ferricyanide with ferric and ferrous chlorides respectively, the author has drawn the conclusion that Prussian blue and Turnbull's blue are two distinct substances of the composition



In support of this view a series of experiments is described showing that the two substances are interconvertible:



If potassium ferrocyanide is added to an excess of ferric chloride and the mixture is then shaken with ferrous chloride, part of the latter is converted into ferric chloride.

A large excess of the ferrous salt, however, is necessary in order to convert Prussian blue into Turnbull's blue to any appreciable extent. On the other hand, if ferric chloride is added to a mixture of potassium ferricyanide and ferrous chloride, it is partly reduced to the ferrous condition.

Prussian blue can be shaken with ferrous chloride without undergoing change, thus indicating that the presence of potassium salts is necessary for the transformation into Turnbull's blue.

Experiments are also described, showing that the same transformation may be effected by reducing Prussian blue with potassium sulphite in the presence of potassium salts.

According to Woringer (A., 1912, i, 170; this vol., i, 504), sodium ferrocyanide differs from potassium ferrocyanide in that it yields with ferric chloride a basic precipitate, corresponding with the composition $\text{Fe}_3(\text{OH})_3[\text{Fe}(\text{CN})_6]_3$, this conclusion being based on the fact that the ratio $\text{Fe}^{\text{III}} : \text{Fe}^{\text{II}}$ in the precipitate is considerably less than the value (0.75) corresponding with the composition $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$.

The author has repeated Woringer's observations and finds that the behaviour of sodium ferrocyanide towards ferric chloride is very similar to that of the potassium salt. In both cases when the ferrocyanide is in excess, the ratio $\text{Fe}^{\text{III}} : \text{Fe}^{\text{II}}$ is greater than 0.75, indicating the presence of sodium or potassium in the precipitate.

On the other hand, when the ferric chloride is in excess, the ratio, in the case of sodium ferrocyanide, is slightly less than 0.75. This discrepancy has not yet been satisfactorily explained, but experiments are described showing that it is probably to be referred to the presence of chlorine in the precipitate and not to the formation of a basic compound as is assumed by Woringer. F. B.

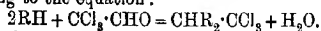
Constitution of the Benzene Nucleus with Reference to the Phenomenon of Di-substitution. BERNARD FLÜRSCHHEIM (*Chem. News*, 1914, 110, 1—2).—A reply to Horton (*A.*, 1914, i, 508). It is pointed out that the special hypotheses advanced to account for the influence of the aldehyde, carbonyl and other unsaturated groups on substitution are quite unnecessary and also erroneous. According to the present author's theory, it is an unsaturated atom attached directly to the benzene nucleus that directs entering groups into the ortho- and para-positions, and this condition is not fulfilled by the carbon atom of the carbonyl group which has much less available affinity left for its union with the nucleus than has, say, the carbon atom of a methyl group, since an increased demand is made on its affinity by combination with an unsaturated atom (bivalent oxygen, trivalent nitrogen, etc.). The fact that the carbon in carbon monoxide is less unsaturated than the carbon in methylene gives independent evidence on this point.

G. F. M.

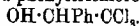
Action of Chloral, Chloral Hydrate, and Bromal on Certain Organic Compounds in the Presence of Aluminium Chloride. G. B. FRANKFORTER and W. KRITCHEVSKY (*J. Amer. Chem. Soc.*, 1914, 36, 1511—1529).—In promoting the condensation of organic substances, aluminium chloride not only plays the part of a catalyst in eliminating hydrogen chloride, but may act as a substitute for sulphuric acid, removing water from the reacting components. Its applicability as a dehydrating agent appears to be almost as universal as that of sulphuric acid, and the authors have employed it in preparing condensation products of the aliphatic, benzene, naphthalene, and anthracene series, not only with chloral, but also with chloral hydrate and bromal. The substances described below have been prepared by the following general method. Aluminium chloride is gradually added to the two reacting components at or below 0°, the mixture is kept for twenty-four to seventy-two hours in a freezing mixture, water is then added, the unchanged substances are removed by distillation with steam, and the condensation product is, in most cases, removed by extraction with ether; in a few cases, the substance must be distilled in a vacuum before it can be crystallised.

Pentane and chloral react very violently; the product is a mixture of substances which is being investigated, but is evidently produced by dehydration.

Benzene, toluene, and xylene yield with chloral the same condensation products as are obtained by means of other condensation reagents, formed according to the equation:



The behaviour of benzene and chloral in the presence of aluminium chloride under the authors' conditions is especially interesting because in 1905, Dienesmann, employing the same substances under somewhat similar conditions, obtained phenyltrichloromethylcarbinol,

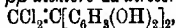


In the case of benzene and toluene under the authors' conditions, dichlorophenylacetaldehyde hydrochloride and the corresponding *p*-tolyl homologue respectively are also produced. Cymene reacts quite

differently from the three preceding aromatic hydrocarbons with chloral, but the products have not been isolated in a pure state.

Ethyl alcohol and chloral react in the cold, with or without the presence of aluminium chloride, to form trichloroacetal, but when the chloride is added at the ordinary temperature, the reaction yields, in addition, acetaldehyde. Benzyl alcohol, chloral, and aluminium chloride at the ordinary temperature yield benzaldehyde and a mixture of two or more chlorinated (unidentified) substances. Phenol in the cold yields trichlorodi-*p*-hydroxyphenylethane.

Resorcinol and chloral in cold carbon disulphide are converted by aluminium chloride into $\beta\beta$ -dichloro- $\alpha\alpha$ -diresorcyloethylene,



light brown powder, which forms a *tetra*-acetate. Anisole yields trichlorodianisylethane, m. p. 78° (Elbs gives 92°), which is reduced to *pp'*-dimethoxystilbene by zinc and alcoholic ammonia, is converted into $\beta\beta$ -dichloro- $\alpha\alpha$ -dianisylethylene, $\text{CCl}_2\text{C}(\text{C}_6\text{H}_4\cdot\text{OMe})_2$, m. p. 109°, by alcoholic potassium hydroxide, and yields trichloro-octanitrodianisylethane, m. p. 173°, yellow crystals, by the action of nitric acid (D 1.5), at 0°. Phenetole yields quite analogous compounds; trichlorodiphenetylethane, $\text{CCl}_2\text{CH}(\text{C}_6\text{H}_4\cdot\text{OEt})_2$, m. p. 105°, colourless, hexagonal crystals, dichlorodiphenetylethylene, m. p. 97°, needles, and trichloro octanitrodiphenetylethane, m. p. 137°, yellow needles.

Phenetole, bromal, and aluminium chloride yield tribromodiphenetylethane, m. p. 112°, yellow crystals (octanitro-derivative, m. p. 153°, yellow crystals). Reaction does not occur when aluminium bromide is used in place of the chloride. Phenyl ether, chloral, and aluminium chloride do not yield well-defined products, benzophenone apparently does not react at all, and acetophenone yields an unidentified substance, b. p. 176°/40 mm.

Benzoic acid does not react with chloral and aluminium chloride. Acetic acid, however, yields a product which, by treatment with ether (not water) to remove the impurities, leaves a residue consisting of a substance, $\text{Al}_2\text{Cl}(\text{OAc})_2\text{CCl}_2\cdot\text{CHO}$, light yellow powder; the chloral is removed from this by cold alcohol. C. S.

Action of Trioxymethylene on Various Hydrocarbons in the Presence of Aluminium Chloride. GEO. B. FRANKFORTER and V. R. KOKATNUR (*J. Amer. Chem. Soc.*, 1914, **36**, 1529—1537).—The action of trioxymethylene is different from that of formaldehyde on hydrocarbons in the presence of aluminium chloride.

By the gradual addition of aluminium chloride to a mixture of benzene and trioxymethylene at 0°, and the decomposition of the product by ice-water, a mixture is obtained from which have been isolated toluene in small amount and diphenylmethane and anthracene in very good yields and in approximately equal molecular proportions. The reaction may be represented by the equation $4\text{C}_6\text{H}_6 + (\text{CH}_2\text{O})_3 = \text{CH}_2\text{Ph}_2 + \text{C}_{14}\text{H}_{10} + 3\text{H}_2\text{O} + \text{H}_2$. The reaction with toluene under similar conditions (below 65°) is quite similar, the products containing benzene and toluene in small amount and also ditolylmethane and dimethylantracene, m. p. 225—226°. The interaction of *o*-xylene, trioxymethylene, and aluminium chloride below 65° leads in the prece-

ing manner to the formation of a mixture of substances, from which have been isolated benzene and possibly some toluene, a *disilylmethane*, b. p. 311—313°, which is highly fluorescent, and a *tetramethylanthracene*, $C_{18}H_{18}$, decomp. 233—235°, yellow, pearly, monoclinic plates, which can be sublimed and forms solutions with an intense green fluorescence.

Mesitylene and trioxymethylene, under the influence of aluminium chloride below 50°, yield, after treatment of the initial product with water, a *tetramethylanthracene*, m. p. 286—287°, a pale yellow, crystalline powder, benzene, toluene, xylene, dimesitylmethane, and durene.

C. S.

2-Chloro-*m*-dinitrobenzene. W. BORSCHKE and D. RANTSCHKEFF (*Annalen*, 1914, 406, 101).—The m. p. of 2-chloro-*m*-dinitrobenzene is 88°, not 92°, as previously stated (*A.*, 1911, i, 329).

C. S.

Desmotropism of Nitro-compounds and Nitro-ketones KURT H. MEYER and PETER WERTHEIMER (*Ber.*, 1914, 47, 2374—2384).—The bromine titration method, which has helped in the investigation of keto-enol isomerism, has been applied to the study of the desmotropic phenomena connected with nitro-derivatives.

As an example, the isomerisation of phenylisonitromethane in alcoholic solution to the true nitro-derivative may be quoted. The solution to be titrated was treated with a trace of ferric chloride, and 0.1*N*-bromine water was added until the deep colour disappeared. The equilibrium mixture contains the merest traces of the *aci*-form, and the transformation is accelerated by strong acids and is almost instantaneous in the presence of sodium acetate. Nitroethane was also dissolved in alkali, and the *aci*-form liberated by the required amount of acid and studied as above. Here, again, there is no appreciable quantity of the *aci*-compound in the equilibrium mixture, but *p*-nitrophenylnitromethane gradually changes in solution, to a certain extent, into the *aci*-form. In pyridine, the equilibrium mixture contains about 16% of the *aci*-compound, in methyl alcohol 0.21%, in ethyl alcohol 0.18%, and in dilute methyl alcohol 0.79%. Comparing this with keto-enol isomerism, a fundamental difference is apparent. Whereas the enolic form of, say, ethyl acetoacetate is favoured least by water, more by methyl alcohol, and still more by ethyl alcohol, the reverse is the case with isonitro-compounds. This is in accordance with the rule that the proportions of the isomerides depend on their solubilities in the medium, for enols are less soluble than ketones in water, but *aci*-compounds are more soluble than true nitro-derivatives. Thus, on acidifying an aqueous solution of ethyl sodioacetoacetate, the liquid is turbid and becomes clear, but on acidifying an alkaline solution of phenylnitromethane, the liquid is first clear and becomes cloudy.

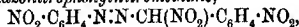
The study of phenyldinitromethane was rendered more accurate by reason of the fact that the bromo-derivative reacts quantitatively with potassium iodide and can therefore be titrated like ethyl bromoacetoacetate. The equilibrium is influenced by solvents in the above manner, there being 15% of the *aci*-form in 30% methyl-alcoholic solution. Nitroacetic ester does not react with ferric chloride, and

scarcely so with bromine, but nitromalonic ester reacts, not immediately, but very quickly. The fact that bromonitromalonic ester reacts at once with potassium iodide, whilst bromonitroacetic ester does not, is not regarded as due to a difference in constitution. They are the extremes of a series of bromo-ketones, aldehydes and nitro-compounds, in which widely different activities towards potassium iodide are displayed by the bromine atoms.

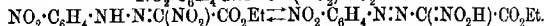
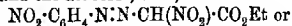
Old alcoholic solutions of ω -nitroacetophenone react with ferric chloride or bromine, but not so the fresh solutions, and the bromonitro-derivative can be titrated iodometrically. The equilibrium mixture contains an amount of the labile form which rises from 2.7% in 67% methyl alcohol to 9–10% in indifferent solvents. This corresponds with keto-enol and not with nitro-desmotropism, and, therefore, the labile form in solution is the nitro-enol and not the *aci*-ketone.

Experiments were also carried out which show that nitro-compounds and nitro-ketones react towards diazonium salts in their labile forms. The free derivatives couple very slowly, but the addition of catalysts, like sodium acetate, leads to very speedy combination.

p-Nitrobenzeneazobenzonitrophenylnitromethane,



forms orange-yellow crystals, m. p. 166°, and *ethyl benzeneazobenzonitroacetate*, $\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{CH}(\text{NO}_2)\cdot\text{CO}_2\text{Et}$, forms orange-yellow crystals, m. p. 60°, and absorbs a little bromine in alcoholic solution. *Ethyl p-nitrobenzeneazobenzonitroacetate* forms long, yellow needles, m. p. 153° (decomp.), and gives yellow solutions in neutral or acid media and red solutions in aqueous or alkaline solvents. The red solutions absorb bromine, and therefore represent equilibria between the azo- or phenyl-hydrazone form and the *aci*-form, thus,



p-Nitrobenzeneazobenzonitroacetophenone, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{CHBz}\cdot\text{NO}_2$, forms pale yellow crystals, m. p. 137°, which give yellow solutions in neutral or acid media and deep red in alkaline or alcoholic solvents.

J. C. W.

Morphological Studies of Benzene Derivatives. VI. Parasulphonic Derivatives of Chloro-, Bromo-, Iodo-, and Cyanobenzene. C. S. MUMFERY (*Proc. Roy. Soc.*, 1914, [A], 90, 455–462).—The sulphonyl chlorides of the three acids containing halogen form an isomorphous series.

$\text{C}_6\text{H}_4\text{Cl}\cdot\text{SO}_2\text{Cl}$: m. p. 53.5°; monoclinic crystals; [$a:b:c = 0.840:1:2.079$; $\beta = 83^\circ 31'$].

$\text{C}_6\text{H}_4\text{Br}\cdot\text{SO}_2\text{Cl}$: m. p. 74.5°; [$a:b:c = 0.820:1:2.074$; $\beta = 83^\circ 13'$].

$\text{C}_6\text{H}_4\text{I}\cdot\text{SO}_2\text{Cl}$: m. p. 84°; [$a:b:c = 0.839:1:2.074$; $\beta = 84^\circ 38'$].

The following sulphonyl bromide is not isomorphous with the above three compounds.

$\text{C}_6\text{H}_4\text{Cl}\cdot\text{SO}_2\text{Br}$: m. p. 56°; monoclinic; [$a:b:c = 1.901:1:1.527$; $\beta = 88^\circ 28'$].

The two following sulphonamides form monoclinic isomorphous crystals from acetone.

$C_6H_4Cl \cdot SO_2 \cdot NH_2$: m. p. 143.5° ; [$a:b:c=0.629:1.0:603$; $\beta=82^\circ 12'$].

$C_6H_4Br \cdot SO_2 \cdot NH_2$: m. p. 165° ; [$a:b:c=0.628:1.0:601$; $\beta=81^\circ 4'$].

The sulphanilides have not been completely measured. Their melting points are: $C_6H_4Cl \cdot SO_2 \cdot NHPh$, 104° ; $C_6H_4Br \cdot SO_2 \cdot NHPh$, 118° ; $C_6H_4I \cdot SO_2 \cdot NHPh$, 143° .

The sulpho-*p*-toluidides form triclinic crystals.

$C_6H_4Cl \cdot SO_2 \cdot NH \cdot C_6H_4 \cdot CH_3$: m. p. 87° ; [$a:b:c=1.020:1.1:1.096$; $\alpha=106^\circ 6'$; $\beta=93^\circ 50'$; $\gamma=77^\circ 29'$].

$C_6H_4Br \cdot SO_2 \cdot NH \cdot C_6H_4 \cdot CH_3$: m. p. 94° ; $C_6H_4I \cdot SO_2 \cdot NH \cdot C_6H_4 \cdot CH_3$: m. p. 129° .

p-Cyanobenzenesulphonic acid was prepared from sulphanilic acid by diazotising and treating the diazo-anhydride with a cold solution of cuprous cyanide. Of the derivatives of this acid, the sulphonyl chloride and sulphonamide were measured.

$CN \cdot C_6H_4 \cdot SO_2Cl$: m. p. 109° ; rhombic; [$a:b:c=1.139:1.1:709$].

$CN \cdot C_6H_4 \cdot SO_2 \cdot NH_2$: m. p. 167° ; rhombic; [$a:b:c=0.793:1.0:537$].

The three following magnesium salts form a well-defined monoclinic isomorphous series.

$(C_6H_4Cl \cdot SO_2)_2Mg, 6H_2O$: [$a:b:c=3.6870:1.0:9223$; $\beta=93^\circ 12'$].

$(C_6H_4Br \cdot SO_2)_2Mg, 6H_2O$: [$a:b:c=3.7380:1.0:9094$; $\beta=93^\circ 51'$].

$(C_6H_4I \cdot SO_2)_2Mg, 6H_2O$: [$a:b:c=3.7965:1.0:9148$; $\beta=93^\circ 11'$].

E. H. R.

New Compound of Mercuric Acetate and Aniline. L. VECCHIOTTI (*Gazzetta*, 1914, 44, ii, 34–38).—2:4-Dimercurioaniline acetate, $NH_2 \cdot C_6H_3(Hg \cdot OAc)_2$, obtained by the interaction of aniline and aqueous mercuric acetate, forms mammillary masses of white prisms, m. p. 206° . The action of acetic anhydride converts it into 2:4-dimercurioacetanilide acetate (compare Pesci, A., 1899, i, 908), which gives 2:4-dibromoacetanilide when treated with bromine. 2:4-Dimercurioaniline hydroxide, $NH_2 \cdot C_6H_3(Hg \cdot OH)_2$, forms microscopic, white needles decomposing at 250° .

T. H. P.

Preparation of Arylcarbamic Esters. FARBERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 272529).—Esters of arylcarbamic acids may be obtained by the interaction of either (1) alkylamines and derivatives of arylcarbamic acids, or (2) aliphatic amines and halogenated alkyl esters of arylcarbamic acids; they exhibit anaesthetic properties.

Diethylaminoethanol phenylcarbamate, obtained from diethylaminoethanol and phenylcarbimide, is a colourless oil with a marked alkaline reaction; its *hydrochloride*, m. p. 143° , picrate, and ferrocyanide were prepared.

Diethylaminoethanol p-ethoxyphenylcarbamate, prepared from diethylaminoethanol and *p*-ethoxyphenylurethane, forms strongly alkaline crystals, and its *hydrochloride*, colourless crystals, m. p. 167° .

Diethylaminoethanol phenylmethylcarbamate, colourless crystals, giving a neutral aqueous solution, and its *hydrochloride*, m. p. 136° ; *diethylaminoethanol diphenylcarbamate*, and its *hydrochloride*, m. p. 180° ; *piperidinoethanol phenylcarbamate*, an oil, and its *hydrochloride*, m. p.

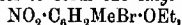
205—207° (decomp.); *piperidinoisopropanol phenylcarbamate*, an oil, and its *hydrochloride*, m. p. 75—77°; *diethylaminoisopropanol phenylcarbamate*, a liquid, and its *hydrochloride*, m. p. 143°; *diethylamino-trimethylcarbinol phenylcarbamate*, m. p. 94°, and its syrupy *hydrochloride*; *tetramethyldiaminopropanol phenylcarbamate*, a colourless, viscous oil, and its *dihydrochloride*, m. p. 226° (decomp.); *diethylamino-dihydroxypropane phenylcarbamate*, m. p. 105—107°, and its *hydrochloride* were also prepared.

T. H. P.

Manufacture of Ethers of Monohydric Phenols and of Neutral and Acid Ethers from the Chlorinated Substitution Products Corresponding with Aromatic Hydrocarbons. CHARLES FORLEY and OSKAR MATTER (Fr. Patent, 457843).—Ethers of monohydric phenols and normal and hydroxylated ethers of polyhydric phenols are prepared by heating chloro-derivatives of aromatic hydrocarbons in a closed vessel with alkali phenoxides or alkylloxides. When polychloro-derivatives are used and a deficit of phenoxide or alkyloxide is taken, chlorinated ethers are obtained. The presence of copper sometimes accelerates the reaction.

T. H. P.

6-Bromo-4-nitro-*m*-cresol and Some of its Derivatives. L. CHAS. RAIFORD and GLADYS LEAVELL (*J. Amer. Chem. Soc.*, 1914, 36, 1498—1511).—In 1889, Claus and Hirsch obtained by the bromination of 4-nitro-*m*-cresol a substance, m. p. 93°, which was stated to be 2:6-dibromo-4-nitro-*m*-cresol. It is now shown that the bromination in glacial acetic acid at the ordinary temperature produces a monobromo-compound, which is rapidly precipitated, and 2:6-dibromo-4-nitro-*m*-cresol, m. p. 87°, which remains in the mother liquor and is precipitated by water. The constitution of the latter has been definitely proved by one of the authors and Stieglitz in 1911, who prepared it from 2:4:6-tribromo-*m*-cresol; so Claus and Hirsch's compound, m. p. 93°, cannot have the constitution ascribed to it by these investigators. The present paper deals mainly with the monobromo-compound mentioned above, which is proved to be 6-bromo-4-nitro-*m*-cresol by the evidence recorded below. It has m. p. 126°, crystallises in yellow plates, is slowly volatile with steam, yields 2:6-dibromo-4-nitro-*m*-cresol, m. p. 87°, by further bromination, and forms the following salts: *ammonium*, orange needles; *potassium*, deep red crystals; *sodium*, red needles, and *silver*, dark red solid. The last salt reacts with ethyl iodide in ether to form the *ethyl ether*,



m. p. 124°, almost colourless crystals.

An alcoholic solution of 6-bromo-4-nitro-*m*-cresol is reduced by boiling concentrated hydrochloric acid and stannous chloride to the *hydrochloride*, almost colourless needles, of 6-bromo-4-amino-*m*-cresol, m. p. 145°, almost colourless crystals.

The nitration of 6-bromo-4-nitro-*m*-cresol by nitric acid, D 1.43, and concentrated sulphuric acid yields, by warming, 2:4:6-trinitro-*m*-cresol, or, at the ordinary temperature, 6-bromo-2:4-dinitro-*m*-cresol, m. p. 77°, yellow needles (*ammonium* salt, orange crystals; *potassium* salt, scarlet plates; *silver* salt, scarlet crystals; *ethyl ether*, m. p. 64—65°, almost colourless crystals).

The chlorination of 6-bromo-4-nitro-*m*-cresol in carbon tetrachloride in the presence of iron produces 2-chloro-6-bromo-4-nitro-*m*-cresol, m. p. 80°, yellow needles (potassium salt, crimson, rhombic crystals). By reduction, the latter yields 2-chloro-6-bromo-4-amino-*m*-cresol, m. p. 145—146°, almost colourless scales (diacetyl derivative, m. p. 199°, colourless needles), which is converted into a diazo-oxide, $C_6H_3ON_2ClBr$, decomp. above 155°, brown needles, by the action of nitrous acid on its hydrochloride. The diazo-oxide is converted by the Sandmeyer method with some difficulty into 2:4-dichloro-6-bromo-*m*-cresol, m. p. 65°, fawn-coloured needles, which is oxidised to 2:4-dichlorotoluquinone by chromic acid. The formation of a dichlorinated quinone proves that the bromine atom in the original bromonitro-*m*-cresol must be in the para-position to the hydroxyl group. C. S.

Aminohydroxyethylbenzene [β -Hydroxy- α -phenylethylamine]. A. KÖTZ and H. SCHNEIDER (*J. pr. Chem.*, 1914, [ii], 90, 136—140).—On reduction with sodium and alcohol, β -oximino- β -phenylethyl alcohol, $OH \cdot N : CPh \cdot CH_2 \cdot OH$, is converted into a mixture of β -hydroxy- α -phenylethylamine and α -phenylethylamine, which may be readily separated by distillation in steam, the last-named base being much more readily volatile than the amino-alcohol.

β -Hydroxy- α -phenylethylamine, $NH_2 \cdot CHPh \cdot CH_2 \cdot OH$, has b. p. 261°, m. p. between 50° and 60°, and forms a hydrochloride, m. p. 146—147°, a carbamide, m. p. 167.5°, and a *N*-benzoyl derivative, m. p. 150°, which, when heated with acetic anhydride and sodium acetate, yields β -benzoyl-amino- β -phenylethyl acetate, m. p. 118°; the *N*-dichloroacetyl derivative, obtained by the interaction of ethyl dichloroacetate and the amino-alcohol in alcoholic solution, crystallises in white scales.

α -Phenylethylamine forms a hydrochloride, m. p. 158°, acetyl derivative, b. p. 287°, carbamide, m. p. 137°, and a monomethyl derivative.

F. B.

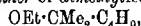
Preparation of Ethers from Aldehyde or Ketone Acetals and Organo-magnesium Compounds. A. E. TSCHITSCHIBABIN and S. A. JELGASIN (*Ber.*, 1914, 47, 1843—1853).—It was recently shown (this vol., i, 276) that the alkyloxy groups in acetals may be replaced by the radicle of an organo-magnesium compound. This reaction is now applied to the preparation of ethers. Formaldehyde acetals yield ethers of primary alcohols, whilst ethers of secondary alcohols are derived from other aldehyde acetals and ethers of tertiary alcohols from ketone acetals. The assumption that the replaceability of the alkyloxy group depends on the degree of saturation of the oxygen atom is justified, for the acetals of formaldehyde, in which the affinity of the carbon atom of the methylene group must make considerable demands on the residual affinity of the oxygen atoms, are the least reactive, whilst ketone acetals react so readily that both alkyloxy groups are frequently displaced.

As a rule, the clear, ethereal solution of the organo-magnesium compound was dropped into the warm acetal, the solvent being allowed to distil off. In the case of methylal and ethylal this procedure was not practicable, and sealed tubes were sometimes used. Many attempts

were made to cause them and isobutylal to react with magnesium benzyl chloride. A grey powder was obtained which seemed to be a complex of the reagents, for it reacted vigorously with water, or when heated above 150° . On working up the products, it was found that below 150° scarcely any replacement of alkyloxy had taken place, whilst at higher temperatures both groups seemed to be engaged with the formation of complex hydrocarbons.

Ordinary acetal, however, reacted with magnesium phenyl bromide on the water-bath to give a 50% yield of the ethyl ether of phenyl-methylcarbinol, $\text{CHMePh}\cdot\text{OEt}$, whilst with magnesium isobutyl bromide it yielded the ethyl ether of methylisobutylcarbinol, $\text{OEt}\cdot\text{CHMe}\cdot\text{C}_4\text{H}_9$, as a liquid with an intense terpene-like odour, b. p. $121-122^{\circ}$ (corr.), D_4^{20} 0.7767, D_{18}^{20} 0.7612, and with magnesium benzyl chloride it formed the ethyl ether of benzylmethylcarbinol, $\text{OEt}\cdot\text{CHMe}\cdot\text{CH}_2\text{Ph}$, as an oil with an intense nerol-like odour, b. p. $205-206^{\circ}$, D_4^{20} 0.9305, D_{18}^{20} 0.9159. 4-Methylcyclohexanol was converted into the bromide, b. p. $70^{\circ}/13$ mm., by the action of hydrogen bromide at 100° , and the magnesium compound of this was added to acetal. The lowest fraction of the product, b. p. 101° , contained apparently methylcyclohexene, and the highest, b. p. $240-252^{\circ}$, dimethyldicyclohexyl, whilst the expected ethyl ether of 4-methylcyclohexyl-methylcarbinol, $\text{OEt}\cdot\text{CHMe}\cdot\text{C}_6\text{H}_{10}\text{Me}$, a liquid with an odour of aniseed, had b. p. $197-198^{\circ}/752$ mm., D_4^{20} 0.8711, D_{18}^{20} 0.8564.

The authors found it difficult to prepare pure acetone acetal, but obtained over 70% yields by the following means. A few drops of sulphuric acid were added to a mixture of acetone (1 mol.), ethyl orthoformate (1 mol.) and pure alcohol (3 mols.), and, after a day, the liquid was made alkaline with ammonia, diluted with ether, and poured into very dilute ammonia. It reacted with magnesium isobutyl bromide, but the yield of the ethyl ether of dimethylisobutylcarbinol,



was only 10-15%. This ether has b. p. $140-142^{\circ}$, D_4^{20} 0.7964, D_{18}^{20} 0.7833, and a pronounced odour of dipentene. J. C. W.

The History of the Quinocarbonium Theory. F. KERNMANN and F. WENTZEL (*Ber.*, 1914, 47, 2274-2275).—A claim to the authorship of the quinocarbonium theory as to the structure of the triphenylcarbinol salts (*A.*, 1901, i, 638) in reply to a statement of Schlenk and Marcus (this vol., i, 823) ascribing this theory to Gomberg. D. F. T.

Cholesterol. XIX. β -Cholestanol. A. WINDAUS and CL. UIBERG (*Ber.*, 1914, 47, 2384-2388).—Many attempts have been made to reduce the unsaturated sterols to the naturally-occurring, saturated sterols, as represented by coprosterol, but hitherto without success. The authors showed (*A.*, 1913, i, 969) that " α -cholestanol," the compound obtained by boiling cholesterol with sodium and amyl alcohol, is really an amyl derivative. The substance obtained by catalytic reduction, namely, dihydrocholesterol or β -cholestanol, is, however, a normal product, but it is not identical with a known, natural, saturated sterol. The authors have now succeeded in con-

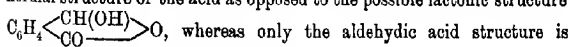
verting cholesterol into coprosterol by chemical means, and in demonstrating the nature of the isomerism existing between β -cholestanol and coprosterol. It is proposed to publish the results in a series of papers, as the subject is complicated. In the present communication, some new derivatives and a new isomeride of β -cholestanol are described.

The following esters of β -cholestanol were prepared: *propionate*, $C_{30}H_{52}O_2$, from the anhydride, four- and six-sided crystals, m. p. 123–124°; *formate*, $C_{28}H_{48}O_2$, from the pure acid, long, narrow tablets, m. p. 83–84°; *benzoate*, $C_{34}H_{52}O_2$, from the anhydride, aggregates of needles, m. p. turbid at 135°, clear at 155°, and *cinnamate*, $C_{30}H_{54}O_2$, from the chloride, tablets, m. p. 160–161°, and again at 192°. β -Cholestanol was also oxidised by chromic acid in 90% acetic acid at 60°, and the ethereal extract separated into β -cholestanone, m. p. 128–129°, and the corresponding dicarboxylic acid, $C_{30}H_{46}O_4$. The latter forms narrow tablets, m. p. 196°, and its *dimethyl* ester, rectangular leaflets, m. p. 66–67°, was prepared by the agency of diazomethane.

β -Cholestanol was found to suffer rearrangement to the extent of about 10% on boiling with sodium in amyl alcohol. After removing the solvent in steam, the residue was a solid which gave a precipitate with alcoholic digitonin solution. This consisted of the compound of the unchanged β -cholestanol. The filtrate was concentrated, shaken with ether, and the extract washed several times with water. This aqueous extract was evaporated to dryness and the residue crystallised from alcohol, when ϵ -cholestanol was obtained in spikes, m. p. 181–182°, $[\alpha]_D^{25} + 33.95^\circ$. It gives the same colour reactions as β -cholestanol and forms the same ketone, but it is less soluble than its stereoisomeride.

J. C. W.

Some Fatty-Aromatic Glycols. H. SIMONIS and P. REMMERT (*Ber.*, 1914, 47, 2307–2311).—By the action of organo-magnesium compounds in excess on phthalaldehydic acids, using anisole as solvent (Simonis and Remmert, this vol., i, 270), dihydric alcohols of the general formula $OH \cdot CHR \cdot C_6H_4 \cdot CR_2 \cdot OH$ can be obtained. This result is interesting, as the formation of α -methylphthalide from *o*-phthalaldehydic acid and magnesium methyl iodide in ethereal solution (Simonis, Marben and Mermod, A, 1906, i, 32) is not decisive for the normal structure of the acid as opposed to the possible lactonic structure



compatible with the results now obtained.

The general method of procedure was to prepare the organo-magnesium compound as usual in ethereal solution, and then to introduce the aldehydic acid dissolved in hot anisole. On evaporating off the ether, a clear solution was finally obtained which, after heating, was submitted to further treatment in the ordinary manner.

The reaction between *o*-phthalaldehydic acid and magnesium ethyl bromide under these conditions produced *o*-*hydroxypropylphenyldiethylcarbinol*, $OH \cdot CHEt \cdot C_6H_4 \cdot CEt_2 \cdot OH$, a colourless oil, b. p. 173°/10 mm., which solidified in needles on a cold day. As is general with the com-

pounds now described, acetic anhydride affects only one hydroxyl group, presumably the secondary one; the *acetyl* derivative is a colourless oil, b. p. 171°/12 mm. When the dihydric alcohol is heated with hydrochloric acid in acetic acid solution for several hours, dehydration takes place with formation of *triethylphthalan* [1:3:3-*triethyl*-1:3-di-*hydroisobenzofuran*], $C_6H_4 \begin{smallmatrix} \text{C} \text{Et}_2 \\ \text{CH} \text{Et} \end{smallmatrix} O$, a pale yellow oil, b. p. 115—118°/10 mm.

*iso*Phthalaldehydic acid and magnesium ethyl bromide give *m-a-hydroxypropylphenyldiethylcarbinol*, a colourless oil, b. p. 174—177°/10 mm.; *acetyl* derivative, b. p. 178—180°/10 mm. When kept in acetic acid solution saturated with hydrogen bromide at 15°, for three days in the dark, one of the hydroxyl groups undergoes esterification, the product, *m-a-bromopropylphenyldiethylcarbinol*, $CHBrEt \cdot C_6H_4 \cdot CEt_2 \cdot OH$,

being an oil.

Terephthalaldehyde and magnesium ethyl bromide react, giving *p-a-hydroxypropylphenyldiethylcarbinol*, an oil, b. p. 186°/15 mm.; the *acetyl* derivative, b. p. 191°/14 mm., and the *p-a-bromopropylphenyldiethylcarbinol*, an oil, were also prepared. D. F. T.

The Constitution of Dypnopinacone and its Derivatives. M. DELACRE (*Ann. Chim.*, 1914, [ix], 2, 63—100).—A résumé of work already published (compare A., 1892, 994; 1900, i, 603; 1902, i, 774; 1904, i, 32; 1912, i, 30; Terlinck, 1905, i, 129). W. G.

The Catalytic Decomposition of Benzoic Acid. PAUL SABATIER and A. MAILHE (*Compt. rend.*, 1914, 159, 217—220).—The authors have tried the effect of various catalytic agents on the decomposition of benzoic acid by heat. A stream of benzoic acid vapour, obtained by bubbling carbon dioxide through the molten acid, was passed over a column of the catalyst at 500 or 550°. Cerium and zirconium oxides and the blue oxides of tungsten and molybdenum are without action, whilst barium oxide merely combines with the benzoic acid. Reduced copper at 550° readily converts benzoic acid into carbon dioxide and benzene. The same decomposition is brought about by cadmium, zinc or titanium oxides and much more slowly and incompletely by thorium, chromium or aluminium oxides. Lithium carbonate produces carbon dioxide, equal amounts of benzophenone and benzene, and a small amount of anthraquinone. Calcium carbonate and manganous oxide have the same effect, but, in the case of the latter, benzene is the predominant product. Reduced nickel or nickel oxide decomposes the acid vapours at 550°, giving carbon dioxide and benzene, which then undergoes rapid dehydrogenation, yielding carbon in a voluminous form and an abundant amount of a mixture of carbon dioxide, hydrogen and methane. Reduced iron has an effect intermediate between that of copper and reduced nickel, the products being benzene with a little diphenyl and the products of dehydrogenation of the benzene. Ferric oxide is first reduced to the metallic state, giving rise to phenol in this process, and then behaves as reduced iron. Ferrous oxide is similarly reduced to the metallic state, but does not produce phenol. W. G.

Additive Compounds of Organic Acids in Pairs. JAMES KENDALL (*J. Amer. Chem. Soc.*, 1914, **36**, 1722—1734).—In an earlier paper (this vol., i, 858) it was shown by means of the f. p. method that many organic acids form additive compounds with dimethylpyrone and that these compounds should be regarded as true oxonium salts. It was also shown that the degree of dissociation, or, in other words, the relative stability of the salt, is a function of the strength of the acid used.

A study has now been made of the f.-p. curves of a series of weak organic acids with certain strong acids. The weak acids employed were benzoic, *o*-, *m*- and *p*-toluic, phenylacetic, cinnamic, acetic, and crotonic acids, and the strong acids were trichloro-, dichloro-, and chloro-acetic acids. The results show that the tendency towards the formation of additive compounds depends on the difference in the strengths of the two acids used. Acids widely divergent in strength give additive compounds which can be readily isolated, whilst acids of similar strength show little tendency to form compounds.

The reaction is regarded as an oxonium salt formation which may be represented thus: $R \cdot C(OH) : O \pm + HX \rightleftharpoons R \cdot C(OH) : O \begin{smallmatrix} H \\ \diagup \\ X \end{smallmatrix}$. This view is fully supported by the quantitative results obtained. E. G.

Hydrogenation of Compounds with Aliphatic Ethylenic Linkings in the Presence of Nickel under Moderate Pressure. ANDRÉ BROCHET and MAURICE BAUER (*Compt. rend.*, 1914, **159**, 190—192).—Using the method already described (compare Brochet, this vol., i, 645) the authors have hydrogenated a number of aromatic compounds containing an ethylenic linking in the side-chain and one aliphatic compound. Δ^1 -Octene readily yields octane. Cinnamic acid, its sodium salt and its methyl ester yield phenylpropionic acid and its corresponding derivatives. The hydrogenation proceeds better with the sodium salt than with the free acid. Piperonylacrylic acid hydrogenates less readily than cinnamic acid, but the conversion readily takes place on using the sodium salt. Anethole, eugenol, and safrole readily undergo hydrogenation at 60—80°, whilst for *isoeugenol* the ordinary temperature suffices. W. G.

Hydrogenation under Atmospheric Pressure in the Presence of Nickel of Compounds with Aliphatic Ethylenic Linkings. ANDRÉ BROCHET and ANDRÉ CABARET (*Compt. rend.*, 1914, **159**, 326—329).—The substances containing aliphatic ethylenic linkings which were hydrogenated in the presence of active nickel under a slightly increased pressure by Brochet and Bauer (preceding abstract) also undergo hydrogenation under atmospheric pressure, but in this case the reaction takes place far more slowly and requires a larger amount of the catalyst. W. G.

Some Nitro- and Amino-derivatives of Salicylonitrile (*o*-Cyanophenol). H. COUSIN and V. VOLMAR (*Compt. rend.*, 1914, **159**, 329—331).—To a cooled solution of salicylonitrile in three times its weight of acetic acid an equal weight of nitric acid in its own weight

of acetic acid is gradually added. A rapid action takes place, two nitro-compounds being formed, which can be separated by fractional dilution. The first to be precipitated on the addition of water is 6-nitrosalicylonitrile, which crystallises from alcohol in golden-yellow prisms, m. p. 132—133°, giving a *potassium* salt in the form of orange-coloured, prismatic needles. Its constitution has been proved by hydrolysis with potassium hydroxide, 6-nitrosalicylic acid being obtained. The second nitro-compound precipitated by water is 4-nitrosalicylonitrile (compare Meyer and Bone, 1893, i, 469). Both nitro-compounds have been reduced by tin and hydrochloric acid, yielding the corresponding amino-compounds. 6-Aminosalicylonitrile crystallises in flattened prisms, m. p. 145° (decomp.), giving a *hydrochloride*, slender, white needles decomposing at 130°. 4-Aminosalicylonitrile crystallises in slender, white needles, m. p. 158—160° (decomp.), giving a *hydrochloride*, prismatic plates, decomposing at 180°. Both bases rapidly become coloured on exposure to light, and they are both diazotised by nitrous acid at 0°, giving diazo-compounds capable of combining with amines and phenols. W. G.

Some Reactions of Mercuric Salicylate. W. OCHSNER DE CONTINCK (*Rev. gén. Chim. pure appl.*, 1914, 17, 125—126).—Mercuric salicylate is decomposed by water, methyl or ethyl alcohol, and acetone at their respective b. p.; it is partly decomposed by water or alcohol even at room temperature. After repeated evaporation with boiling water and washing the product with water at 0° until the filtrate has a neutral reaction, the normal salt is converted into *basic mercuric salicylate*, $C_6H_4 \begin{smallmatrix} \diagup CO_2 \\ \diagdown O \end{smallmatrix} Hg$, decomp. 239—240°, amorphous, white powder, which is insoluble in the usual solvents and in the moist state is decomposed by heat into mercury, carbon dioxide, phenol, and oxygen. C. S.

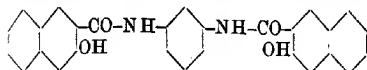
Palladosalicylates. G. A. BARBIERI (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 880—885).—In continuation of the previous work (this vol., ii, 375), which showed the existence of palladous acetylacetonate, analogous to the corresponding cupric salt, the author has now prepared palladosalicylic acid and several of its salts, which are similar to the cuprisalicylates obtained by Ley and Erler (*A.*, 1908, i, 177).

T. H. P.

Crystals of α -Ethoxy- α -diphenylacetic Acid. A. JOHNSON (*Centr. Min.*, 1914, 430).—The compound, $OEt \cdot CPh_2 \cdot CO_2H$, melting at 114°, crystallises in colourless, anorthic tablets; [α : β : ϵ = 1.7019:1.08166; α = 72°3', β = 116°2', γ = 120°40']. There are good cleavages parallel to {100}, {010} and {001}, the other forms observed being {110} and {101}. E. H. R.

Preparation of Arylamides of 2-Naphthol-3-carboxylic Acid. CHEMISCHE FABRIK GRIESHEIM-ELEKTRO (Fr. Patent, 464448).—Arylamides of 2-naphthol-3-carboxylic acid may be obtained by heating the acid with the corresponding arylamines and a dehydrating

agent, such as phosphorus trichloride or thionyl chloride, in an different liquid (compare this vol., i, 48). The following compounds, all of which give yellow solutions in sodium hydroxide solution, have been prepared: *anilide*, m. p. 243—244°; *o-aniside*, m. p. 167—168°; *o-chloroanilide*, m. p. 225—226°; *p-chloroanilide*, m. p. 258—259°; *m-chloroanilide*, m. p. 241—242°; 2:5-dichloroanilide, m. p. 246—247°; *o-toluidide*, m. p. 195—196°; *p-toluidide*, m. p. 221—222°; α -*naphthalide*, m. p. 222—223°; β -*naphthalide*, m. p. 243—244°; the compound (annexed formula), prepared from tolylene-2:4-diamine, m. p. 261—262°; *ethylanilide*, m. p. 153—154°, and the *o-hydroxyanilide*, m. p. 214—215° (decomp.). The above melting points are uncorrected.



T. H. P.

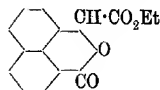
Manufacture of Salts of Acetylsalicylic [*o*-Acetoxybenzoic] Acid. OTTO GERNGROSS and HERMANN KAST (Fr. Patent, 464081).—An aqueous solution or suspension of *o*-acetoxybenzoic acid is stirred or shaken with an oxide, hydroxide, carbonate, etc., the mixture being cooled if necessary and the solution being then evaporated in a vacuum and the *o*-acetoxybenzoate separated.

T. H. P.

The Acid Salts of Dibasic Acids. É. JUNGLEISCH and PH. LANDRIEU (*Ann. Chim.*, 1914, [ix], 2, 5—56).—A résumé of work already published (compare this vol., i, 13, 416, 657).

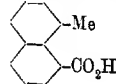
W. G.

peri-Derivatives of Naphthalene. VI. G. ERRERA and G. AJON (*Gazzetta*, 1914, 44, ii, 92—98).—In view of the ease with which *peri*-naphthindantrione and dihydroxyketoperinaphthindene undergo oxidation and reduction in presence of alkali (compare A., 1913, i, 985), the authors have investigated the action of sodium carbonate on the alcoholate of the triketone.



The products obtained comprise: (1) *ac-naphthaquinone*; (2) *ethyl naphthalidecarboxylate* (annexed formula), which crystallises in colourless needles or faintly brownish-yellow prisms, m. p. 108—109°. The corresponding *acid*, $C_{13}H_8O_3$, which may also be obtained by reduction of naphthalonic acid (compare Errera and Cuffaro, A., 1912, i, 273), forms minute, colourless needles, m. p. 210—212°. When heated above its melting point, the acid yields *naphthalide* (annexed formula), which crystallises in yellow needles, m. p. 159—160°, and has an oxygen ring even more stable than that of phthalide.

Methyl naphthalonate, $C_{13}H_8O_3Me$, hard, almost colourless, crystals, m. p. 130—131°, which redden in the light, and the *ethyl ester*, $C_{13}H_8O_3Et$, colourless needles or faintly brown prisms, m. p. 94—95°, were prepared.



8-Methylnaphthoic acid (annexed formula), obtained, together with a little naphthalidecarboxylic acid and aceraphthene, by vigorous reduction of naphthalonic acid with hydriodic acid and phosphorus, forms small, hard prisms or white, flexible needles, melting indefinitely at 130—131°.

T. H. P.

Some Dipeptides of Hydroxybenzoic Acids and of Syringaic Acid. RICHARD LEPSIUS (*Annalen*, 1914, 406, 11—21).—The following dipeptides have been prepared by Fischer's general method: *m*-Methylcarbonatobenzoic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}_2\text{Me}$, m. p. 151° (corr.), colourless needles, prepared by the action of cold *N*-sodium hydroxide (2 mols.) and methyl chlorocarbonate (1.1 mol.) on *m*-hydroxybenzoic acid and subsequent acidification, forms with phosphorus pentachloride a chloride, m. p. 63° , colourless needles, which reacts with cold aqueous *m*-hydroxybenzoic acid and *N*-sodium hydroxide (2 mols.) to form 3-*m*-methylcarbonatobenzoxyloxybenzoic acid,

$\text{CO}_2\text{Me}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, m. p. 169° (corr.), colourless needles. The last substance forms a chloride, $\text{C}_{16}\text{H}_{11}\text{O}_6\text{Cl}$, m. p. 91 — 92° (corr.), and is converted into 3-*m*-hydroxybenzoxyloxybenzoic acid, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, m. p. 199° (corr.), by cold *N*-ammonia and subsequent acidification.

The following substances have been prepared by similar methods: 4-*m*-methylcarbonatobenzoxyloxybenzoic acid, m. p. 201° (corr.), and its chloride, m. p. 105 — 106° (corr.); 4-*m*-hydroxybenzoxyloxybenzoic acid, m. p. 239 — 240° (corr.), with preliminary slight decomp.; 3-*p*-methylcarbonatobenzoxyloxybenzoic acid, m. p. 185° (corr.), and its chloride, m. p. 120° (corr.); 3-*p*-hydroxybenzoxyloxybenzoic acid, m. p. 254° (corr.); methylcarbonatosyringaic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{O}\cdot\text{CO}_2\text{Me}$, m. p. 191 — 192° (corr.), and its chloride, m. p. 123 — 124° (corr.); ethylcarbonatosyringaic acid, m. p. 182 — 183° (corr.), and its chloride, m. p. 75° ; methylcarbonatodisyringaic acid,

$\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{O}\cdot\text{CO}_2\text{Me}$, m. p. 223 — 224° (corr.); disyringaic acid, m. p. 260° (corr.); 4-methylcarbonatosyringaoxyloxybenzoic acid, m. p. 203° (corr.), and its chloride, m. p. 150 — 151° (corr.); 4-syringaoxyloxybenzoic acid, m. p. 208° (corr.); *p*-methylcarbonatobenzoxyloxybenzoic acid, m. p. 228 — 229° (corr.), and its chloride, m. p. 138° (corr.); *p*-hydroxybenzoxyloxybenzoic acid, m. p. 282 — 284° (decomp. corr.). C. S.

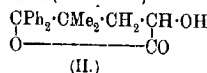
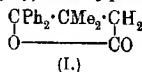
Stability of Cinnamaldehyde. H. ADIE PHILLIPS (*Pharm. J.*, 1914, 93, 129—130).—Under the usual conditions prevailing during steam-distillation, cinnamaldehyde, both in the pure state and as a constituent of cinnamon oil, is not oxidised to any appreciable extent.

W. P. S.

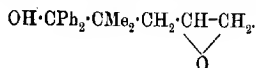
Syntheses by means of Sodamide. Propylenedimethylacetophenone Oxide [$\delta\epsilon$ -Oxido- β -benzoyl- β -methylpentane] and Some of its Derivatives. New Method of Preparing γ -Ketonic Acids. A. HALLER and (Mme.) RAMART-LUCAS (*Compt. rend.*, 1914, 159, 143—149. Compare this vol., i, 695, 968).— $\delta\epsilon$ -Oxido- β -benzoyl- β -methylpentane or its dimeride (*loc. cit.*) on oxidation in acetic acid with chromic acid in amount sufficient to furnish 1 atom of oxygen, yields β -benzoyl- β -methylpentane- $\delta\epsilon$ -diol, m. p. 100° (*loc. cit.*). If enough chromic acid is used to supply 4 atoms of oxygen, the product in each case is β -benzoyl- β -methylbutyric acid, $\text{CMe}_2\text{Bz}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, m. p. 100° . This substance is obtained similarly by the oxidation of $\alpha\alpha$ -dimethyl- α -allylacetophenone by means of chromic acid in acetic acid solution.

On treating a mixture of a ketone and chloroacetic acid with sodium ethoxide (compare Darzens, A., 1905, i, 116) or with sodamide (compare Claisen, A., 1905, i, 286) a glycidic ester is obtained. Thus phenyl isopropyl ketone and chloroacetic acid yield ethyl isopropylphenylglycidate, which on saponification yields the corresponding acid, m. p. 73°. If, however, iodo- or bromo-acetic acids are used in place of chloroacetic acid an ester is obtained, b. p. 168—175°/15 mm., which on saponification yields an acid identical with β -benzoyl- β -methylbutyric acid. This method can be generalised for the preparation of a series of γ -ketonic acids.

On condensing $\delta\epsilon$ -oxido- β -benzoyl- β -methylpentane with magnesium phenyl bromide a compound is obtained, crystallising from light petroleum in needles, m. p. 107—108°, and from ether in prisms, m. p. 122°. Analysis shows it to have the composition $C_{19}H_{22}O_3$. It yields an acetyl derivative, slender needles, m. p. 119·5°, and a phenylurethane, m. p. 116—117°. On oxidation with chromic acid in acetic acid in the cold, it yields a compound, $C_{19}H_{20}O_3$, m. p. 155—156°, whilst, if the oxidation is carried out at the boiling point, the product is a compound, $C_{18}H_{18}O_3$, m. p. 146—147°. The latter compound can be synthesised by the condensation of magnesium phenyl bromide with ethyl β -benzoyl- β -methylbutyrate, thus proving its constitution to be that of $\gamma\gamma$ -diphenyl- $\beta\beta$ -dimethyl- γ -butanolide (formula I), whilst that of the compound $C_{19}H_{20}O_3$ is $\delta\delta$ -diphenyl- $\gamma\gamma$ -dimethylpentan- α -ol- γ -olide (formula II).

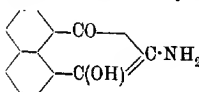


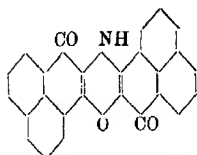
From this it follows that the compound, m. p. 107—108°, obtained by the condensation of magnesium phenyl bromide and $\delta\epsilon$ -oxido- β -benzoyl- β -methylpentane, is $\delta\epsilon$ -oxido- $\beta\beta$ -dimethyl- $\alpha\alpha$ -diphenylpentan- α -ol,



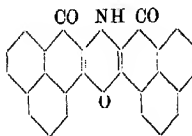
W. G.

Aminohydroxyketoperinaphthindene. V. G. ERRERA (*Gazzetta*, 1914, 44, ii, 18—24).—The compound obtained by the action of phenylhydrazine on hydroxyketoperinaphthindene (compare A., 1911, i, 465; 1913, i, 985) has now been purified and is shown to be aminohydroxyketoperinaphthindene (annexed formula), which crystallises in shining, golden-brown leaflets, m. p. 260° (decomp.), and is coloured faintly violet by hot water, and more intensely so by alkali carbonates. Solutions of alkali hydroxides dissolve it, giving deep violet solutions, from which acids apparently precipitate the original compound. In sulphuric acid it forms a yellow or reddish solution according to the concentration of the acid. In hot benzaldehyde it is very readily soluble, the solution depositing an additive product (I) in orange needles on cooling. When subjected to prolonged treatment with boil-



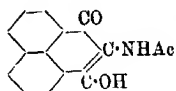


or



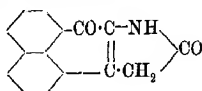
ing alcohol containing 10% of sulphuric acid, it yields the annexed compound, which forms bluish-black needles

or plates, not melting even at 300°.

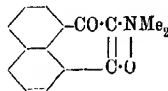


The corresponding *acetylamino*-derivative (annexed formula) forms orange needles, m. p. 191—192°, and yields an *anhydro*-compound (I.) in yellow needles, m. p. 185—186°, or in reddish-yellow plates or needles containing

benzene of crystallisation; its solutions in alcohol or acetic acid show faint green fluorescence.



(I.)



(II.)

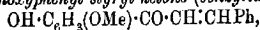
When treated with methyl sulphate in alkaline aqueous solution, the amino-compound is converted into the *betaine* derivative (II), which forms brownish-yellow, opaque laminæ, m. p. 187—188°, with a faint odour of trimethylamine; its hydrochloride forms yellow needles.

T. H. P.

Chalkones and Hydrochalkones [Phenylstyryl Ketones and Phenyl Phenylethyl Ketones]. IV. G. BARGELLINI and LYDIA MOSCI (*Gazzetta*, 1914, 44, ii, 25—34).—Further hydrogenated chalkones have been prepared by the method of reduction previously described (A., 1913, i, 59). The same method is applied to the analogous compound, dihydroxybenzylidenecumarone, with which, although the chromophore group, $\cdot\text{CO}\cdot\text{C}\cdot\text{C}\cdot$, exists partly in a ring, only the double

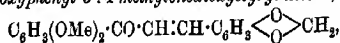
linking becomes saturated, the carbonyl group remaining unaltered.

2-Hydroxy-4-methoxyphenyl styryl ketone (benzylidenæpæonol),



prepared by the interaction of benzaldehyde and 2:4-dihydroxyacetophenone monomethyl ether (pæonol) in alcoholic solution in presence of sodium hydroxide (compare Emiliewicz and von Kostanecki, A., 1898, i, 369), forms yellow crystals, m. p. 106—108°. On reduction it yields 2-hydroxy-4-methoxyphenyl phenylethyl ketone, m. p. 103—104°. In Bargellini and Marantonio's paper (A., 1908, i, 801), the melting points of the mono- and di-methyl ethers of 2:4-dihydroxyphenyl phenylethyl ketone should be interchanged.

3:4-Dimethoxyphenyl 3:4-methylenedioxyphenyl ketone,



prepared from 3:4-dimethoxyacetophenone and piperonaldehyde,

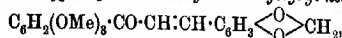
forms pale yellow crystals, m. p. 140—142°, and gives an intense red coloration with concentrated sulphuric acid.

3:4-Dimethoxyphenyl 3:4-methylenedioxyphenylethyl ketone,



forms white, woolly needles, m. p. 98—100°.

3:4:5-Trimethoxyphenyl 3:4-methylenedioxyacetyryl ketone,



prepared from 3:4:5-trimethoxyacetophenone (compare Mauthner, A., 1910, i, 680) and piperonaldehyde, forms pale yellow crystals, m. p. 118—120°, and gives a red solution in concentrated sulphuric acid.

3:4:5-Trimethoxyphenyl 3:4-methylenedioxyphenylethyl ketone,

$\text{C}_{19}\text{H}_{16}\text{O}_6$, forms colourless leaflets, m. p. 96—98°.

2:3:4-Trimethoxyphenyl 3:4-methylenedioxy styryl ketone,

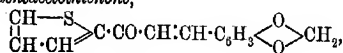


similarly prepared from 2:3:4-trimethoxyacetophenone (compare Blumberg and von Kostanecki, A., 1903, i, 644; Mannich and Hahn, A., 1911, i, 648), forms yellow, prismatic needles, m. p. 97—98°, gives a red solution in concentrated sulphuric acid, and on reduction yields the corresponding hydrochalkone, which is an oil and decomposes when an attempt is made to purify it by distillation.

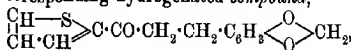
2-Hydroxy-4-methoxyphenyl styryl ketone (compare Woker, von Kostanecki, and Tambor, A., 1904, i, 184), m. p. 98°, may be prepared by the action of sodium hydroxide on 7:8-dimethoxyflavanone, m. p. 114—115°, into which it is reconverted by the action of acid. This transformation of a flavanone into a chalkone would appear to be of general character, although only one other instance of such a change has been previously observed (compare Perkin and Hummel, T., 1904, 85, 1459).

2-Hydroxyphenyl 3:4-dimethoxystyryl ketone, $\text{C}_{17}\text{H}_{14}\text{O}_4$, forms shining, white needles, m. p. 80—82°.

Piperonylideneacetothienone,



prepared from piperonaldehyde and acetothienone in presence of alcoholic sodium hydroxide, forms pale yellow scales, m. p. 127—129°, and gives a red solution in concentrated sulphuric acid. On reduction it yields the corresponding hydrogenated compound,



which forms white, tabular crystals, m. p. 50—52°, and is coloured dark garnet-red, but is not dissolved, by concentrated sulphuric acid.

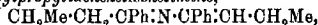
Dihydroxybenzylcumarone, $\text{C}_6\text{H}_2(\text{OH})_2 \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{CH} \cdot \text{CH}_2\text{Ph}$, obtained

by reduction of the corresponding dihydroxybenzylidenecumarone, m. p. 221°, forms pale yellow crystals, m. p. about 120° (+ $\frac{1}{2}\text{H}_2\text{O}$), or dirty white crystals, m. p. 160—164° (anhydrous). T. H. F.

Some Ketisoketimines. CHARLES MOUREU and GEORGES MIGNONAC (*Compt. rend.*, 1914, 159, 149—152. Compare this vol., i, 830).—The

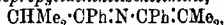
authors have prepared a number of *ketisoketimines* by heating the corresponding *ketimines* at 115° in a current of hydrogen for several days and separating the products by fractional distillation. They are all very viscous oils, coloured more or less deeply greenish-yellow, and having a slight odour. They are decomposed by hydrochloric acid, yielding one molecule of ammonia and two molecules of the corresponding ketone. They do not evolve gas on treatment with magnesium ethyl bromide.

Diphenylpropylpropylideneketisoketimine,



b. p. $200^\circ/12$ mm.; $D_4^{25.5-29}$ 0.9958; $n_D^{25.5-29}$ 1.5809.

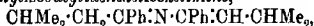
Diphenylisopropylisopropylideneketisoketimine,



b. p. $144-145^\circ/4$ mm., obtained from *phenylisopropylketimine*,
 $\text{NH:CPh}\cdot\text{CHMe}_2$,

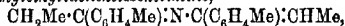
b. p. $98-100^\circ/8$ mm.

Diphenylisobutylisobutylideneketisoketimine,



b. p. $186-187.5^\circ/7$ mm.; D_4^{25} 0.9674; n_D^{25} 1.5617.

Di-p-tolyethyllethylideneketisoketimine,



b. p. $178-179^\circ/2.5$ mm., obtained from *p-tolyethylketimine*,
 $\text{NH:C}(\text{C}_6\text{H}_4\text{Me})\cdot\text{CH}_2\text{Me}$,

b. p. $94-96^\circ/2.5$ mm.; $D_4^{25.5}$ 0.9805; $n_D^{25.5}$ 1.5448.

Diphenylbenzylbenzylideneketisoketimine, $\text{CH}_2\text{Ph}\cdot\text{CPh:N}\cdot\text{CPh:CHPh}$,

b. p. $248-250^\circ/2$ mm., obtained from *phenylbenzylketimine*,
 $\text{NH:CPh}\cdot\text{CH}_2\text{Ph}$,

white crystals, m. p. 57° .

W. G.

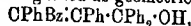
Reaction Between Magnesium Phenyl Bromide and Unsaturated Compounds Containing a Number of Phenyl Groups. DOROTHY A. HAHN and RUBY MURRAY (*J. Amer. Chem. Soc.*, 1914, 36, 1484—1497).—Highly phenylated compounds containing phenyl groups in the α - and β -positions to a carbonyl group offer much greater resistance to the attack of magnesium phenyl bromide than substances containing the same number of phenyl groups in the α -position only; thus tetraphenylpropanone does not react at all, while benzpinacol reacts fairly readily. In order to ascertain whether other negative groups exert a similar steric effect, the behaviour of $\alpha\beta$ -dibenzoylstyrene and of $\alpha\beta$ -dibenzoylstilbene towards magnesium phenyl bromide has been examined. The result shows that the introduction of a phenyl group in the β -position to a carbonyl group causes resistance to the addition of magnesium phenyl bromide in the 1:4 position ($\text{O:C}^1\text{C}^2\text{C}^3\text{C}^4$); in agreement with this, Kohler has observed that α -benzoylstilbene reacts quantitatively and additively in the 1:4 position with magnesium phenyl bromide, whilst tetraphenylpropanone, as stated above, does not react at all.

The reaction between $\alpha\beta$ -dibenzoylstyrene and ethereal magnesium phenyl bromide leads, after the usual treatment, to the formation of $\alpha\beta$ -dibenzoyl- $\alpha\beta$ -diphenylethane, m. p. 256° , and 2:3:4:5-tetra-

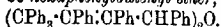
phenylfuran, m. p. 175° (accompanied by their respective products of oxidation, $\alpha\beta$ -dibenzoylstilbene, m. p. 212°, and dihydroxytetraphenylfuran, m. p. 157°); these two substances are evidently formed by the rearrangement and the dehydration respectively of a primary product, $\text{CHPhBz}\cdot\text{CPh}\cdot\text{CPh}\cdot\text{OH}$, resulting from dibenzoylstyrene by addition in the 1:4 position.

$\alpha\beta$ -Dibenzoylstilbene is conveniently obtained in quantity by the following method. The dry ethereal solution containing the additive compound of $\alpha\beta$ -dibenzoylstyrene and magnesium phenyl bromide is slowly treated with bromine (1 mol.), and the mixture is treated at once with ice and hydrochloric acid, when dibenzoylstilbene is immediately precipitated.

The reaction between $\alpha\beta$ -dibenzoylstilbene and ethereal magnesium phenyl bromide in the cold leads to the formation of two substances, m. p. 208° and 157° respectively. These are produced by addition in the 1:2 position and are regarded as geometrical isomerides,



for the following reasons: first, either of the two products can be obtained in an average yield of 80% by modifying the conditions of the preparation; secondly, each of the substances, dissolved in acetic anhydride, forms an equilibrium mixture from which both can be isolated by crystallisation; thirdly, the two substances yield identical products of reduction and of oxidation. Thus, γ -benzoyltetraphenyl- Δ^3 -propanol, m. p. 208°, and its isomeride, m. p. 157° (which is the more reactive form), are reduced by stannous chloride and hydrochloric acid, or by hydriodic acid and amorphous phosphorus at 160°, to a substance, $\text{C}_{24}\text{H}_{20}\text{O}$, m. p. 185°, large plates, which is probably *pentaphenylbutenyl oxide*, $\text{O} \begin{array}{c} \text{CPh}_2-\text{CPh} \\ | \\ \text{CHPh}\cdot\text{CPh} \end{array}$; it reacts with ethereal magnesium phenyl bromide to form, ultimately, a substance, $\text{C}_{30}\text{H}_{22}\text{O}$, m. p. 232°, large plates or prisms, which may be *hexaphenylbutenyl ether*,



The oxidation of the two isomerides by hot chromic and acetic acids yields benzoic acid, benzil, benzophenone, and a small amount of a substance, $\text{C}_{27}\text{H}_{22}\text{O}_3$, m. p. 143°. This substance probably has the

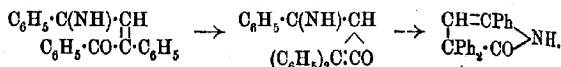
formula $\text{O} \begin{array}{c} \text{CPh}\cdot\text{CPh}_2\cdot\text{OH} \\ | \\ \text{CPh}\cdot\text{OH} \end{array}$, since it yields benzophenone and benzoic

acid by further oxidation and is reduced by stannous chloride and hydrochloric acid to benzaldehyde and triphenylvinyl alcohol. C. S.

Dibenzoylstyrene. E. OLIVIERI-MANDALÀ and E. CALDERARO (*Gazzetta*, 1914, 44, ii, 85—92).—The action of sunlight on dibenzoylstyrene in benzene solution yields the lactone of triphenylcrotonic acid, which is also obtained by heating the same compound at 300° (compare Japp and Tingle, T., 1897, 71, 1138). The action of bromine in the light gives the same tribromotriphenylfuran as was obtained by Japp.

The influence of sunlight does not change the action of alcoholic ammonia on this compound, the resulting product, m. p. 180°, undergoing transformation into the isomeric triphenylpyrrolone,

$\text{NH} \begin{smallmatrix} \text{CPh} \cdot \text{CH} \\ \diagdown \quad \diagup \\ \text{CO} - \text{CPh}_2 \end{smallmatrix}$ (compare Japp and Tingle, *loc. cit.*). In view of the explanation suggested by Schroeter (A., 1909, i, 617) for the benzylic acid transposition, the compound, m. p. 180°, and its conversion into triphenylpyrrolone are represented thus:

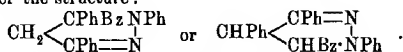


With hydroxylamine, dibenzoylstyrene gives in neutral or alkaline solution a compound, $\text{C}_{22}\text{H}_{17}\text{O}_3\text{N}$, which crystallises in white leaflets or hard needles, m. p. 140—141°, whilst in acid solution, an isomeric compound, crystallising in yellow needles, m. p. 167—168°, is obtained. It is suggested that these compounds are derived from a closed ring, isooxazoline, and that their structures are $\text{N} \begin{smallmatrix} \text{CPh} \cdot \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{O} - \text{CPhBz} \end{smallmatrix}$ and

$\text{N} \begin{smallmatrix} \text{CPh} \cdot \text{CHPh} \\ \diagdown \quad \diagup \\ \text{O} - \text{CHBz} \end{smallmatrix}$ respectively. Such ring compounds might readily be

formed by isomeric change of the oxime, $\begin{smallmatrix} \text{C} \cdot \text{CC} - \\ | \\ \text{NOH} \end{smallmatrix} \rightarrow \begin{smallmatrix} > \text{C} \cdot \text{CH} \cdot \text{C} - \\ | \quad \quad | \\ \text{O} \quad \quad \text{N} \end{smallmatrix}$

The compound described by Japp and Klingemann (T., 1890, 57, 662) as dibenzoylstyrenemonophenylhydrazone is remarkably stable towards the action of acids and the author regards it as a pyrazoline derivative of the structure:



Both the carbonyl groups of dibenzoylstyrene react with semicarbazide, giving the compound, $\text{C}_{24}\text{H}_{22}\text{O}_2\text{N}_6$, m. p. 211—212° (decomp.).
T. H. P.

Certain Derivatives of Iodoanil. C. LORING JACKSON and ELMER KEISER BOLTON (*J. Amer. Chem. Soc.*, 1914, 36, 1473—1484. Compare Torrey and Hunter, A., 1912, i, 475; Jackson and Bolton, this vol., i, 297, 550).—The substances, $\text{C}_6\text{X}_2\text{Y}_2\text{O}_2$ (where X is Br or I, and Y is OMe, OEt, OCH_2Ph , OAc, or $\text{CH}(\text{CO}_2\text{Et})_2$), described in the paper exhibit a surprising resemblance to the corresponding chlorine and bromine compounds; for example, the colour is essentially the same, and the solubilities do not exhibit any qualitative differences. A comparison of the m. p. of corresponding chloro-, bromo-, and iodo-compounds shows that the regularity recorded in two cases by Torrey and Hunter (*loc. cit.*) is not part of a general rule applying to all benzoquinones containing halogens.

The following substances of the type $\text{C}_6\text{X}_2\text{Y}_2\text{O}_2$ are made usually by the action of di-iododiphenoxy-*p*-benzoquinone on the sodium derivative of the alcohol; in making the dimethoxy- and diethoxy-compounds the first products are the hemi-acetals, which change to the quinones by heating with acetic anhydride: X=I, Y=OMe, light red needles, m. p. 196°; X=I, Y=OEt, orange-red needles, m. p. 186°; X=I, Y=O·CH₂Ph, orange-red plates, m. p. 160°; X=Br, Y=O·CH₂Ph,

orange-red plates, m. p. 146° (in making the last two compounds, ethyl alcohol must be completely absent, otherwise the diethoxy-derivative is obtained); $X = I$, $Y = NHPh$, dark purple needles, m. p. 240° (decomp.); $X = I$, $Y = NH \cdot C_6H_4Me(p)$, dark purple plates, decomp. 205° (these two are prepared by heating di-iododiphenoxy-*p*-benzoquinone with alcohol and the necessary amine [rather more than 2 mols.]); $X = I$, $Y = CH(CO_2Et)_2$, yellow, fern-like crystals, m. p. 138° , (*sodio*-derivative, intensely blue); $X = Br$, $Y = CH(CO_2Et)_2$, yellow needles, m. p. 109° . The last substance (and also the preceding) cannot be hydrolysed without decomposing, is reduced to the corresponding *quinol*, $C_6Br_2(OH)_2[CH(CO_2Et)_2]_2$, m. p. 183° , colourless prisms, by phenylhydrazine in toluene, and reacts with bromine in boiling alcohol to form *ethyl dibromo-*p*-benzoquinone dibromomalonate*, $C_6Br_2O_2[CBBr(CO_2Et)_2]_2$, m. p. 172° , yellow needles.

Di-iododiphenoxyquinol, $C_6I_2(OPh)_2(OH)_2$, m. p. 260° , colourless needles, is prepared by reducing di-iododiphenoxy-*p*-benzoquinone with phenylhydrazine in hot glacial acetic acid. *Dibromodiacetoxy-*p*-benzoquinone*, m. p. 205° , yellow plates, is prepared by heating bromoanilic acid and acetic anhydride. *Silver iodoanilate*, $C_6IO_2(OAg)_2$, dark red, amorphous substance, prepared from a dilute solution of iodoanilic acid and a slight excess of silver nitrate, is not attacked by cold concentrated nitric acid. *Di-iododiamino-*p*-benzoquinone*, $C_6I_2O_2(NH_2)_2$, m. p. 230° (decomp.), brown, amorphous solid, obtained by heating iodoanil with an excess of alcoholic ammonia, is easily soluble in cold aqueous sodium hydroxide.

Tetra-iodoquinol, $C_6I_4(OH)_2$, m. p. 258° (decomp., beginning at 238°), cream-coloured crystals, prepared from iodoanil and phenylhydrazine in hot glacial acetic acid, rapidly oxidises in the air. The *diacetate*, m. p. 285° (decomp., beginning at about 270°), colourless needles, is obtained by heating the quinol with acetic anhydride and sodium acetate or iodoanil with acetic anhydride and a few drops of concentrated sulphuric acid. The action of iodine chloride on *p*-benzoquinone suspended in warm carbon tetrachloride results in the formation of dichlorobenzoquinone, m. p. 161° , not the expected iodo-compound.

C. S.

Preparation of Terpenes from their Hydrogen Haloids. ALFRED MEYER (D.R.-P. 272562).—Hydrogen haloids may be removed from their compounds with terpenes, such as pinene and dipentene hydrochlorides, by heating with kieselguhr in the presence or absence of (1) an absorbent of the hydrogen haloid and (2) a diluent.

T. H. F.

Oil of *Ocimum pilosum*, Roxb. KSHITIBHUSAN BHADURI (J. Amer. Chem. Soc., 1914, 36, 1772–1773).—A specimen of the volatile oil of *Ocimum pilosum*, Roxb., prepared from the whole plant by steam distillation, had $D_{20}^{25} 0.8872$, $n_D^{25} 1.4843$, and $\alpha_D -3.7^{\circ}$. The greater part distilled at 205 – 230° , and about 10% of it was absorbed by 5% potassium hydroxide. The oil contained citral (41%), citrovellaldehyde (34%), limonene, cineole, and a little thymol.

E. G.

Oil of Port Orford Cedar Wood and Some Observations on *d*- α -Pinene. A. W. SCHORGER (*J. Ind. Eng. Chem.*, 1914, 6, 631–632).—The Port Orford cedar (*Chamaecyparis lawsoniana Parlatores*) grows on the coastal regions of Oregon and California and yields an oil having the following approximate composition: α -*d*-pinene, 60–61%; dipentene, 6–7%; free *l*-borneol, 11%; esters, as borneol acetate, 11.5%; cadinene, 6–7%; loss, 5%. The combined borneol occurs mainly as borneol acetate, but esters of formic and decolic acid are also present. In the old oil, formic, acetic, and decolic acids occur in the free state. The α -pinene, after purification, yielded the following constants: b. p. 156.0–156.1°; D^{20} 0.8631; n_D^{25} 1.4684; $[\alpha]_D + 51.52^\circ$.
W. P. S.

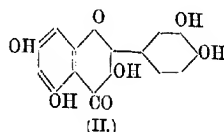
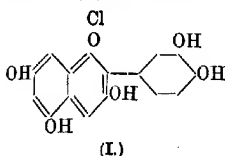
Influence of the Solvent on the Viscosity of Caoutchouc Solutions. F. KIRCHHOF (*Kolloid. Zeitsch.*, 1914, 15, 30–38).—Measurements have been made of the viscosity of solutions containing 0.5, 1, 2, and 3 grams of caoutchouc in 100 c.c. of light petroleum, benzene, carbon tetrachloride, trichloroethylene, tetrachloroethane, and pentachloroethane. In general, the viscosity coefficients run parallel with the numbers which afford a measure of the swelling capacity of the various solvents towards caoutchouc (compare Posnjak, A., 1912, ii, 912). In accordance with Hatschek's views (A., 1913, ii, 559), the observed connexion between the viscosity and swelling capacity is probably determined by the combination of the caoutchouc with the solvent. The extent to which this occurs increases with the magnitude of the viscosity coefficient.
H. M. D.

Isolation of the Insoluble [Substances] in Caoutchouc. GUSTAVE BERNSTEIN (*Kolloid. Zeitsch.*, 1914, 15, 49–50).—The author points out that the method described by Spence and Kratz (this vol., i, 855) for the separation of the insoluble substances in caoutchouc is not novel in so far as it depends on a reduction of the viscosity of caoutchouc solutions. The diminution in viscosity can be brought about in various ways other than by the addition of acids, and furthermore, the addition of sulphuric acid has previously been employed for the estimation of pure caoutchouc in the crude product (compare Marquis and Heim, A., 1913, ii, 884).
H. M. D.

Biochemical Syntheses of β -Monoglucosides of *m*- and *p*-Xylene Glycols. EM. BOURQUELOT and AL. LUDWIG (*Compt. rend.*, 1914, 159, 213–215; *J. Pharm. Chim.*, 1914, [vii], 10, 111–116).—These two glucosides have been prepared by the action of emulsin on a solution of the glycol and dextrose in aqueous acetone. β -*Xyleneglycol glucoside* crystallises in very slender needles, containing $1H_2O$, m. p. 85–95°. The anhydride prepared at 100° has $[\alpha]_D - 46.86^\circ$. β -*p*-*Xyleneglycol glucoside* crystallises in prismatic plates, m. p. 159–160°, $[\alpha]_D - 50.47^\circ$. Both these glucosides are slightly bitter in taste, and are readily hydrolysed by 3% aqueous sulphuric acid or by emulsin in aqueous solution. Neither reduces Fehling's solution.
W. G.

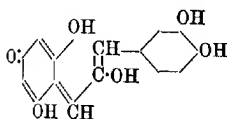
The Relation between Anthocyanins and Flavones.

RICHARD WILLSTÄTTER and HEINRICH MALLISON (*Sitzungsber. K. Akad. Wiss. Berlin.*, 1914, 769—777).—Anthocyanins are glucosides the colour-components of which (anthocyanidins) have recently been recognised as derivatives of phenylbenzopyrylium (Willstätter, this vol., i, 564). The fission of anthocyanidins into phloroglucinol and phenol-carboxylic acids by alkalis leaves undetermined only the position of the phenyl group in the pyrylium nucleus. Thus cyanidin chloride may be a 2- or a 4-phenylbenzopyrylium derivative. The latter formula is improbable because a substituted benzophenone (maclurin) is not produced by the action of warm alkalis. If, therefore, cyanidin chloride is (I) its relation to quercetin (II) suggests that the oxida-



tion of anthocyanins should result in the formation of yellow mordant dyes and, conversely, the reduction of flavonols should yield colouring matters of the anthocyanin group. Observations bearing on these relations have been recorded about fifty years ago by Stein and by Hlasiwetz and Pfaunder, and quite recently by Combes, Everest, Wheldale, and Watson and Sen (*L.*, 1914, 105, 389).

The authors have reduced an alcoholic solution of quercetin by 20% hydrochloric acid, magnesium, and a large quantity of mercury at a temperature not exceeding 0°, whereby a substance, called *allocyanidin chloride*, violet-red, microscopic needles, is obtained. The chloride readily loses hydrogen chloride and yields *allocyanidin*, $C_{15}H_{12}O_6$, which resembles, but is not identical with, cyanidin. *alloCyanidin* is not dihydroquercetin (compare Watson and Sen, *loc. cit.*), but is an



oxonium compound (annexed formula). More important than the examination of *allocyanidin* is the discovery that when the reduction of quercetin by the preceding reagents is effected at 35°, the products are *allocyanidin chloride* and

cyanidin chloride, the latter being identical in all respects with the substance obtained from the cornflower and the rose.

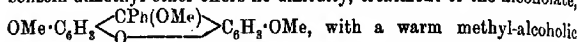
The formation of cyanidin from quercetin has a twofold significance. It is a synthesis of cyanidin, since quercetin has been synthesised by von Kostanecki, Lampe, and Tambor in 1904. Moreover, it proves the constitution of cyanidin chloride (I), establishes almost with certainty the constitutions of the nearly related anthocyanidins, pelargonidin and delphinidin, and leaves for future determination only the orientation of the methyl groups in a number of other anthocyanidins derived from these by the introduction of one or more methyl groups.

It follows from the preceding that an anthocyanidin, in its acid-free form, is isomeric with the flavone derivative which contains in a benzene nucleus one less atom of oxygen.

C. S.

Resorcinolbenzein (3-Hydroxy-9-phenylfluorone). F. KEHRMANN and E. LOTH (*Ber.*, 1914, 47, 2271—2274. Compare Kehrmann, A., 1913, i, 1352; Pope, T., 1914, 105, 251).—The m. p. of the monomethyl ether of resorcinolbenzein is 204°.

Although the preparation of the oxonium bromide of resorcinolbenzein dimethyl ether offers no difficulty, treatment of the alcoholate,



solution of hydrogen chloride gave a yellow, crystalline solid which even after crystallisation from a mixture of methyl alcohol and ether is apparently a mixture of a mono- and a di-hydrochloride. The monohydrochloride was finally obtained almost pure by repeatedly grinding the yellow solid with sodium chloride solution, when it remained as an orange-yellow solid.

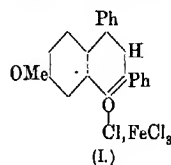
D. F. T.

The Synthesis of Benzopyrylium Salts. HERMANN DECKER and PAUL BECKER (*Ber.*, 1914, 47, 2288—2292. Compare Decker and Fellenberg, A., 1907, i, 950, 1064).—Attempts to replace resorcinol in the synthesis of benzopyrylium salts by phenol have proved unsuccessful, but the monomethyl ether of resorcinol can be applied with satisfactory results.

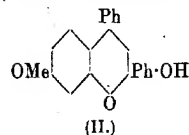
By passing hydrogen chloride into a solution of resorcinol monomethyl ether and dibenzoylmethane in acetic acid, a clear deep red solution can be obtained which, after keeping for three days and precipitating unchanged material by the addition of an equal bulk of 10% hydrochloric acid, gives on treatment with solid ferric chloride an

oily precipitate; this soon crystallises and consists of 7-methoxy-2:4-diphenylbenzopyrylium ferrichloride (formula I), which crystallises from acetic acid in yellow needles, m. p. 186°; the acetic acid solution on the addition of water exhibits a marked yellowish-green fluorescence.

If the ferrichloride is treated with sodium hydroxide solution, ferric hydroxide is precipitated and on passing carbon dioxide through the filtrate a red deposit of a chalkone



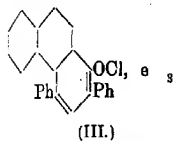
produced, arising from fission of the ring of the primarily produced carbinol (formula II). With hydrochloric acid, the chalkone regenerates the original oxonium salt, whilst further treatment with warm sodium hydroxide solution causes its decomposition into acetophenone and 2-hydroxy-4-methoxybenzophenone.



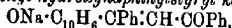
The success of this synthetic process with resorcinol monomethyl ether disposes of the idea that the presence of a hydroxyl group in the para-position is necessary for the reactivity of the hydrogen atom involved in the condensation. On this account the failure of attempts

to effect this synthetic reaction with phenol is probably not due to the absence of the second hydroxyl radicle as much as to the unsubstituted hydrogen atom turning the reaction into a different course. Confirmation of this view is supplied by the possibility of effecting a similar condensation, certainly with some difficulty, with β -naphthol, which possesses no hydrogen atom in the para-position to the reactive hydrogen atom.

An equimolecular mixture of β -naphthol and dibenzoylmethane in alcohol was saturated with hydrogen chloride and heated for two hours in a sealed tube at 100° . After five to six days the deep yellow solution was treated with solid ferric chloride, when



2 : 4 - *diphenylnaphthapyrylium ferrichloride* (formula III) separated in golden-yellow leaflets, m. p. $272-273^\circ$, the yield being poor. Corresponding with this salt there is a colourless carbinol which on boiling with sodium hydroxide solution undergoes conversion into the red sodium salt of *phenyl hydroxynaphthylstyryl ketone*,



the free ketone obtainable by the action of carbon dioxide being recondensed to the oxonium chloride when heated with hydrochloric acid.

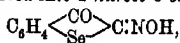
The yellow colour of the benzopyrylium salts is attributed to the CO^+ group, and the postulation of other chromophores such as an ortho- or para-quinonoid configuration is regarded as unnecessary.

D. F. T.

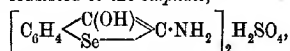
Aromatic Selenium Compounds. III. Selenonaphthenquinone. R. LESSER and A. SCHOELLER (*Ber.*, 1914, 47, 2292—2307. Compare Lesser and Weiss, A., 1913, i, 1184; 1912, i, 642).—The preparation of selenonaphthenquinone, the selenium isologue of isatin, offered some difficulty on account of the sensitiveness of the substance towards most reagents, in which characteristic it resembles the analogous oxygen compound coumarandione. Success was achieved by the application of the method used by Pummerer (A., 1910, i, 510) for isatin and thionaphthenquinone, who condensed indoxyl and 3-hydroxythionaphthen with aromatic nitroso-compounds and then hydrolysed the resulting anils.

In the conversion of *o*-carboxyphenylselenolacetic acid into 3-hydroxy-selenonaphthen by the action of acetic anhydride, it is advisable not to heat above $100-105^\circ$. At the ordinary temperature bromine attacks an acetic acid solution of 3-hydroxyselenonaphthen with formation only of a mono-bromo-derivative, whilst at higher temperatures, oxidation is effected with formation of "selenindigo" [2 : 2'-bisoxyselenonaphthen]. 2-Bromo-3-hydroxyselenonaphthen forms woolly, yellow needles, m. p. 103° ; it decomposes on keeping, and when heated with aniline gives only a resinous product. The action of chlorine on an acetic acid solution of the hydroxyselenonaphthen gave rise to no crystalline product other than "selenindigo."

When treated with the calculated quantity of nitrous acid, 3-hydroxyselenonaphthen is converted into 2-nitroso-3-oxyselenonaphthen,

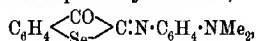


silky, yellow needles, m. p. 154—155°, soluble in most solvents. It is a very stable substance and can be dissolved in warm sulphuric or hydrochloric acid without decomposition; prolonged boiling with 30% sodium hydroxide solution causes the formation of diphenyldiselenodio-carboxylic acid (diselenodisalicic acid). When shaken in sodium carbonate solution with methyl sulphate, the nitroso-oxy-selenonaphthen gives a *methyl* derivative, yellow leaflets with a bronze lustre, m. p. 146—147°; it also forms an *acetyl* derivative, yellow needles, m. p. 177—178°, and a *benzoyl* derivative, yellow leaflets, m. p. 184—185°, but the action of hydroxylamine gave only a *substance* of uncertain nature, yellow needles, m. p. 168° (decomp.). Reduction of the nitroso-compound by various agents followed a quite different course from that observed with the corresponding sulphur compound, and did not lead to the desired selenonaphthenquinone; for example, iron and acetic acid gave a product which, on the addition of sulphuric acid, separated from solution in pale yellow tablets; these slowly decomposed above 200°, and apparently consisted of the *sulphate*,



of a very unstable base; the *hydrochloride* closely resembles the sulphate; *perchlorate*, needles; *ferrichloride*, crystalline.

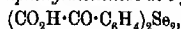
Selenonaphthenquinone-2-p-dimethylaminoanil,



green prisms with metallic lustre, m. p. 166—167°, which give a deep red powder or solution, is slowly formed when a bimolecular proportion of 2*N*-aqueous sodium hydroxide is added to an ice-cold alcoholic equimolecular mixture of 3-hydroxyselenonaphthen and *p*-nitrosodimethylaniline; it is very sensitive towards mineral acids, but a very deliquescent, crystalline, brown *hydrochloride* was prepared. In a similar manner *selenonaphthenquinone-2-anil*, orange-coloured needles or leaflets, m. p. 145—146°, is obtainable from hydroxyselenonaphthen and nitrosobenzene, but a red substance, prisms, m. p. 145—146°, of distinct nature, is concurrently formed in smaller quantity. Both these *anils* when boiled with the calculated amount of phenylhydrazine in acetic acid solution give the same 2-benzeneazo-3-hydroxyselenonaphthen, $\text{C}_6\text{H}_4 \begin{array}{c} \text{C(OH)} \\ \text{Se} \end{array} \text{C}\cdot\text{N}_2\text{Ph}$, orange-red needles, m. p. 207—208°, as is obtained by the interaction of 3-hydroxyselenonaphthen and benzenediazonium chloride; this substance dissolves unchanged in concentrated sulphuric acid, but fuming sulphuric acid converts it into a yellow *sulphonic acid*, the salts of which are red. The above *anils* are also affected analogously by boiling with hydroxylamine hydrochloride in acetic acid solution containing an excess of potassium acetate, the product being the 2-nitroso-3-oxy-selenonaphthen described above.

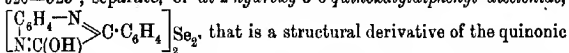
Selenonaphthenquinone-2-anil proved unsuited to the preparation of selenonaphthenquinone, as it is hydrolysed by mineral acids only when heated, under which conditions the quinone is resinified. With care it is possible to hydrolyse selenonaphthendimethylaminoanil in ice-cold ethereal solution by aqueous hydrochloric acid, so that a good yield of

selenonaphthenquinone, $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{Se} \end{smallmatrix} \text{CO}$, is obtained; this substance forms red or sometimes orange-yellow needles, m. p. 102–103°, which dissolve in organic solvents to a reddish-yellow solution, and in sulphuric acid to a red, gradually passing into a green; it gives with coal-tar benzene a more violet indophenin coloration than does isatin. The quinone is decomposed when dissolved in dilute acetic acid, and the action of dilute aqueous solutions of alkali hydroxides is so marked that, in order to prepare the corresponding quinonic acid, it is necessary to take the ethereal solution of the quinone with very dilute, ice-cold sodium carbonate solution; acidification then liberates *selenonaphthenquinonic acid* (*diphenyldiselenide-di-o-glyoxylic acid*),

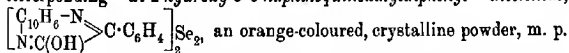


orange-yellow, microscopic prisms, which have no definite m. p., and decompose at 200–285°, according to the rate of heating. Esters of this acid are formed when a solution of the selenonaphthenquinone in a primary alcohol is warmed, and the products are identical with those obtained by direct esterification of the acid; the following esters were examined: *methyl* ester, yellow leaflets, m. p. 157–158°; *ethyl* ester, yellow needles, m. p. 125–126°; *propyl* ester, crystals, m. p. 111–112°. The action of phenylhydrazine on selenonaphthenquinone, and also on the above esters, gave rise to complex mixtures, a small quantity of a substance, prisms, m. p. 72–73°, being separated from the product yielded by the methyl ester.

Towards *o*-diamines, selenonaphthenquinone is more reactive than thionaphthenquinone (Bezdzik, Friedländer and Koeniger, A., 1908, i, 200), and on mixing with an equimolecular proportion of *o*-phenylenediamine in cold ethereal solution, orange-yellow, microscopic needles, m. p. 320–325°, separate, of *di-2-hydroxy-3-o-quinoxalyldiphenyl diselenide*,



that is a structural derivative of the quinonic acid and not of the quinone. In an analogous manner 1:2-naphthylenediamine reacts with the quinone, giving an excellent yield of the corresponding *di-2-hydroxy-3-o-naphthoquinoxalyldiphenyl diselenide*,



an orange-coloured, crystalline powder, m. p. 352–355°. The esters of the quinonic acid also underwent condensation with these *o*-diamines in acetic acid solution containing hydrochloric acid, and the products were the *hydrochlorides* of the preceding, that of *di-2-hydroxy-3-o-quinoxalyldiphenyl diselenide* having m. p. 350–360° (decomp.).

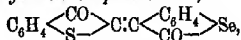
In boiling ethereal solution, selenonaphthenquinone enters into combination with aniline and with *p*-aminodimethylaniline, giving crystalline *substances*, yellow prisms, m. p. 218–219°, and garnet-red prisms, m. p. 226° (decomp.) respectively, the constitution of which, as well as of a substance, red, microscopic prisms, m. p. 205–206° (decomp.), obtained in an analogous manner from thionaphthenquinone and *p*-aminodimethylaniline remains for the present uncertain.

Indigoid dyes were obtained by condensation of selenonaphthenquinone with indoxyl and its isologues, the products being remarkable

for their fusibility; the condensation was effected by the general method of heating the components in equimolecular proportion in acetic acid solution containing a few drops of hydrochloric acid. Indoxyl and the quinone gave "2-indole-3-selenonaphthenindigo"

[2-indoxyl-3-selenonaphthen-2-one], $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{C}:\text{C} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagdown \quad \diagup \\ \text{CO} \end{smallmatrix} \text{Se}$, small, bluish-black prisms, m. p. 241–242°, the chloroform solution of which has a reddish-violet colour with a deep blue fluorescence; fuming sulphuric acid dissolves the substance with violet coloration, producing a red sulphonic acid soluble in water.

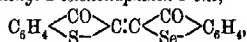
The selenonaphthenquinone and 3-hydroxythionaphthen yielded 3-oxy- Δ^2 -thionaphthenyl-3-selenonaphthen-2-one,



deep reddish-brown needles, m. p. 196–197°, which gives a non-fluorescent deep reddish-violet solution in chloroform and dissolves in fuming sulphuric acid with decomposition.

3-Hydroxyselenonaphthen and the quinone condense together with formation of 2:3'-bisoxyselenonaphthen, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{Se} \end{smallmatrix} \text{C}:\text{C} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagdown \quad \diagup \\ \text{CO} \end{smallmatrix} \text{Se}$ reddish-brown needles, m. p. 186–187°, the chloroform solution of which is violet-red with a blue fluorescence.

3-Oxy- Δ^2 -thionaphthenyl-2-selenonaphthen-3-one,



was obtained by heating an equimolecular mixture of 3-hydroxyselenonaphthen and 2-bromo-3-ketodihydrothionaphthenquinone (Bezdzik Friedländer and Koeniger, *loc. cit.*); it forms deep red needles, m. p. near 350°, and in chloroform gives a violet-red colour with blue fluorescence; fuming sulphuric acid dissolves it to a blue solution which contains a carmine-red sulphonic acid soluble in water.

All these dyes can be sublimed without decomposition, and are easily reduced to rats by sodium hyposulphite in alkaline solution, the yellow solutions restoring the dye on exposure to air or more rapidly on treatment with potassium ferricyanide.

D. F. T.

Alkaloids of Papaver Orientale. WALTER KLEE (*Arch. Pharm.*, 1914, 252, 211–273).—In 1813 Petit stated that *Papaver orientale* contains narcotina, morphine, and meconic acid. The author has been unable to detect any one of the three. Numerous experiments on the plant at different periods of its existence show that at times of vigorous growth thebaine is almost the only alkaloid present in the root. On the contrary, after the period of blooming and the withering of the aerial parts, a phenolic base and only a little thebaine are present.

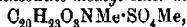
A hot alcoholic extract of the dried, coarsely-powdered roots is diluted with water, the alcohol is evaporated, the fats, resins, and chlorophyll are removed, and the mixture of crude alkaloids (about 0.5% yield) ultimately obtained is readily separated by *N*-sodium hydroxide into a non-phenolic constituent, which is easily identified as thebaine, and a phenolic base. The latter has the formula $\text{C}_{19}\text{H}_{21}\text{O}_3\text{N}$, and is therefore called *isothebaine*.

*iso*Thebaine has m. p. 203—204°, $[\alpha]_D^{18} + 285.1^\circ$, and crystallises in highly refractive, colourless, rhombic crystals $[\alpha:b:c=0.95145:1:1.61846]$, which are somewhat sensitive to light. The *hydrochloride*, easily soluble crystals, *sulphate*, m. p. 120—121° (decomp.), small needles, *nitrate*, and *hydrogen l-tartrate*, clusters of short needles, are described. The colour reactions of the alkaloid are: concentrated sulphuric acid, colourless; Erdmann's reagent, pale yellow; Fröhde's reagent, blue, then green, later, dark olive-green, finally, pale green; Mandelin's reagent, pale olive, then olive-brown. Quite unique among the *Papaveraceae* alkaloids is the behaviour of *isothebaine* with concentrated nitric acid which produces an intense violet coloration, whereby even a trace of the alkaloid can be detected in the presence of a large quantity of thebaine.

*iso*Thebaine contains, in addition to the phenolic hydroxyl group, two methoxy-groups and a methylimino-group. In deciding his line of attack on the problem of the constitution of the alkaloid, the author has been guided by the inference that *isothebaine*, according to its method of occurrence in the plant, is produced from thebaine. It responds to Pellagri's reaction just as do bulbocapnine and *isocorydine*, and also resembles these two alkaloids in forming an optically inactive *diacetyl* derivative, $C_{19}H_{19}O_2NAc_2$, m. p. 80—85°, colourless leaflets, by heating with acetic anhydride and anhydrous sodium acetate. There can be little doubt, therefore, that *isothebaine* contains the ring system of morphothebaine and apomorphine.

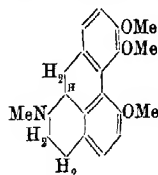
If *isothebaine* is formed from thebaine by rupture of the bridge O-ring and formation of an *isoquinoline* ring, then *isothebaine methyl ether* (assuming the three methoxy-groups are in positions 3:4:6) and morphothebaine dimethyl ether (which is laevorotatory) will be optical antipodes. Morphothebaine and *isothebaine* are practically unattacked by ethereal diazomethane; however, methylation occurs satisfactorily with nascent diazomethane in *isoamyl ether* (Gadamer's method). Neither of the ethers has been obtained in a crystalline state. *Morphothebaine dimethyl ether*, a faintly yellow, resinous substance, has $[\alpha]_D - 184.8^\circ$ in chloroform, and forms a *hydrogen d-tartrate*, m. p. 205° (decomp.), $[\alpha]_D 74.3^\circ$ in water, colourless needles. *iso-Thebaine methyl ether* has $[\alpha]_D + 234.5^\circ$ in chloroform, and forms a *hydrogen l-tartrate*, m. p. 226—227° (decomp.), $[\alpha]_D + 143^\circ$ in water, colourless needles. The two ethers, although showing many similarities in their colour reactions, are obviously not optical antipodes.

It is equally possible that *isothebaine* may be derived from thebaine by rupture of the bridge O-ring, the substituents (2OMe and OH) being in positions 3:5:6. If this is so, the exhaustive methylation of *isothebaine* should yield the trimethoxyphenanthrene obtained from morphothebaine by Paschorr and Rettberg. An aqueous solution or suspension of the sodium derivative of *isothebaine* is converted by methyl sulphate into *isothebaine methyl ether methosulphate*,



m. p. 237—238°, $[\alpha]_D + 158.1^\circ$ in water, glistening needles, which is decomposed by boiling aqueous sodium hydroxide, yielding two *methine* bases. One of these has m. p. 104—105°, $[\alpha]_D - 283.9^\circ$ in ether,

crystallises in stout, colourless needles, and is unsaturated; the other is amorphous and optically inactive. An ethereal solution of the methine bases reacts with methyl sulphate to form *isothebainethine methyl ether dimethosulphate*, $C_{19}H_{19}O_3NMe_2 \cdot SO_4Me$, m. p. 195–196°, colourless needles, which is optically inactive (and is therefore formed from the amorphous methine base) and is converted by warm methyl alcoholic sodium hydroxide into trimethylamine and a *trimethoxyvinylphenanthrene*. The latter in acetone at 0° is oxidised by aqueous potassium permanganate to a *trimethoxyphenanthrenecarboxylic acid*, m. p. 170–171°, faintly yellow needles or leaflets, which loses carbon dioxide by heating with glacial acetic acid at 220° under pressure and yields a *trimethoxyphenanthrene*. The *picrate*, m. p. 160°, dark red needles, of the latter is not identical with the *picrate*, m. p. 109–110°, of 3:5:6 (i.e. 3:4:6)-trimethoxyphenanthrene, but may be the slightly impure *picrate*, (m. p. 166°) of 3:4:5-trimethoxyphenanthrene.



Assuming this to be correct, the exhaustive methylation of *isothebaine* proves that the group $\cdot CH_2 \cdot CH_2 \cdot NMe \cdot$ is attached to the phenanthrene nucleus in positions 8:9 and that the (partly methylated) phenolic groups are in positions 3:4:5. *isothebaine* methyl ether, therefore, has the annexed formula. *isothebaine* itself may have its phenolic hydroxyl group in position 4 or 5, the former being the more probable.

The oxidation of *isothebaine* or of its methyl ether by alcoholic iodine does not yield products which throw any light on the constitution. C. S.

Minor Alkaloids in *Papaver Orientale*. J. GADAMER (*Arch. Pharm.*, 1914, 252, 274–280).—In addition to the two chief alkaloids, thebaine and *isothebaine*, isolated from *Papaver orientale* by Klee (preceding abstract), the author has obtained evidence of the presence of several others in extremely minute quantities. At least three of these are phenolic and two are non-phenolic in character. One of the latter is proved to be protopine by its m. p. 204–205°, crystalline form, and colour reactions; the other was accidentally lost before it had been examined.

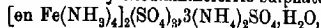
One of the phenolic alkaloids is a *substance*, m. p. about 238–239°, darkening at 209–210°, called *glauclidine*. Its colour reactions are very similar to those of glaucine, and the magnitude of its specific rotation, $[\alpha]_D$ about 50° in chloroform, indicates that it belongs to the glaucine, not the corytuberine, group of alkaloids. By methylation with nascent diazomethane in *isoamyl* ether, it yields a substance which forms a *hydrogen l-tartrate* exhibiting in its crystalline form and colour reactions a very great similarity to glaucine hydrogen *l-tartrate*; it is impossible to say whether or not the two substances are identical, because the amount of the methylated product is too small for analysis and the colour reactions of glaucine and glauclidine are very similar. C. S.

Complex Salts of Iron. III. G. SPACU (*Ann. Sci. Univ. Jassy*, 1914, 8, 162–204. Compare this vol., i, 573).—*Diaquotetrammine*-

ferric sulphate, $[(\text{H}_2\text{O})_2\text{Fe}(\text{NH}_3)_2](\text{SO}_4)_3$, reddish-brown powder, is obtained by the action of a rapid current of dry ammonia on finely powdered, hydrated ferric sulphate for several hours at the ordinary temperature. It readily loses ammonia by exposure to the air, is rapidly decomposed by water with the formation of ferric hydroxide, and is insoluble in most solvents except acetic and dilute sulphuric acid; the sulphate radicle is completely ionisable.

By treating the complex salts of iron containing pyridine, ethylenediamine, etc., which have been previously described (*loc. cit.*), with dry ammonia, the author has observed a partial, or in the case of pyridine generally a total, replacement of the basic molecules by ammonia. Thus hydrated tetrapyridineferric sulphate yields a *tetra-aquopyridine-heptammineferric sulphate*, amorphous, brown powder, to which is given the formula $[(\text{H}_2\text{O})_2\text{Fe Py}(\text{NH}_3)_3][(\text{H}_2\text{O})_2\text{Fe}(\text{NH}_3)_4](\text{SO}_4)_3$; this substance, like the other complex salts of iron containing ammonia, is unstable in the air, and is readily decomposed by water. Hydrated aquotripyridineferrous sulphate is converted by ammonia into hydrated *tetrammineferrous sulphate*, $[\text{Fe}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$, brown, amorphous powder.

Ethylenediamine sulphate and hydrated ferric sulphate react in boiling dilute sulphuric acid to form a white, amorphous substance, $[\text{Fe}_2(\text{en H}_2\text{SO}_4)_2](\text{SO}_4)_2 \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, which reacts quantitatively with barium chloride to produce barium sulphate, and combines additively with dry ammonia (14 mols.) to form a double salt of ammonium sulphate and tetrammine-ethylenediamineferric sulphate,



amorphous, brown powder.

The author gives a list of the 212 complex salts of iron known at the present time and remarks that very rarely does aniline enter into the composition. He describes two such compounds. *Dianilineferrous sulphate*, $[\text{Fe}(\text{NH}_2\text{Ph})_2]\text{SO}_4$, prepared by boiling ferrous sulphate with aniline, is a white, amorphous substance which can be kept in the dark and is hydrolysed by water, yielding ferrous hydroxide and, by oxidation, ultimately ferric hydroxide. *Triaquopentanineferric sulphate*, $[(\text{H}_2\text{O})_3\text{Fe}_2(\text{NH}_2\text{Ph})_5](\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$, prepared by heating aniline and hydrated ferric sulphate on the water-bath, is an amorphous, reddish-brown powder, which can be kept in a desiccator, but is hydrolysed by water.

A mixture of hydrated ferric chloride and an excess of potassium thiocyanate is thoroughly ground in a mortar, at first alone, subsequently with a large excess of pyridine. The product, after being purified and rapidly crystallised from boiling pyridine, is a substance, $[\text{Fe Py}_3](\text{SCN})_6$, brilliant, black needles, which is isomeric with the crystalline, yellow thiocyanate obtained by Grossmann and Hunseler in 1905. The two modifications are relatively stable and can be preserved in an atmosphere of pyridine. The black form is labile, but each can be transformed into the other under suitable conditions; thus the black form changes to the yellow by solution in pyridine, whilst the yellow modification is transformed into the black by chloroform. By heating, the two isomerides lose pyridine at different rates; in both cases, the last molecule of pyridine is removed only

with difficulty above 250°. The two substances behave alike towards ammonia, yielding very hygroscopic products which are probably hexamineferrous thiocyanate, $[\text{Fe}(\text{NH}_2)_6](\text{SCN})_2$, and towards chlorine water, whereby they are oxidised to ferric salts. The author discusses the nature of the isomerism of the yellow and the black thiocyanates and inclines to the opinion that they are *cis* and *trans* stereoisomerides of the type $[\text{MA}_2\text{B}_4]$.

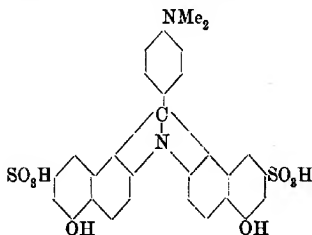
C. S.

Preparation of a Derivative of 2-Phenyl-6-methylquinoline-4-carboxylic Acid of Therapeutic Application. CHEMISCHE FABRIK AUF ARTEN (VORM. E. SCHERING) (Swiss Patent, 64348).—*Methyl 2-phenyl-6-methylquinoline-4-carboxylate*, prepared from the acid by the ordinary methods of esterification, forms white needles, m. p. 91°, yields salts with acids, and has the advantage of tastelessness over the acid itself.

T. H. P.

Preparation of Acridine Derivatives from Aminohydroxynaphthalenesulphonic Acids. FARBER & VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 272612).—These derivatives are prepared by the action in the warm of tertiary aromatic amines and formaldehyde, in presence of dilute mineral acid, on 1-aminohydroxynaphthalenesulphonic acids with the 2-position

unoccupied or on 2-aminohydroxynaphthalenesulphonic acids with the 1-position unoccupied. They are of value for the preparation of colouring matters of various groups.



The compound (annexed formula), prepared from 2-amino-5-hydroxynaphthalene-7-sulphonic acid, dimethylaniline and formaldehyde, forms an orange-

red, crystalline powder. The analogous compound, obtained from 2-amino-6-hydroxynaphthalene-8-sulphonic acid, diethylaniline and formaldehyde is orange-yellow and the compound from 1-amino-5-hydroxynaphthalene-7-sulphonic acid, dimethylaniline and formaldehyde, olive-green. The colorations given by these compounds with various reagents are described.

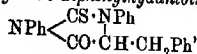
T. H. P.

Hydantoins. XXVIII. Synthesis of 1:3:4-Trisubstituted Hydantoins from Ethyl Anilinomalonate. TREAT B. JOHNSON and NORMAN A. SHEPARD (*J. Amer. Chem. Soc.*, 1914, **36**, 1735—1743).—During the course of a study of the condensation of hydantoins with aldehydes, it was found that certain hydantoins do not undergo such condensation (Wheeler and Hoffman, A., 1911, i, 500). On investigating some of these cases, results were obtained which rendered it desirable to develop a method for preparing 1:3:4-trisubstituted hydantoins which would not involve the condensation of an aldehyde with a hydantoin. An account of such a method is now given.

Diethyl benzylanilinomalonate, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{NHPh})(\text{CO}_2\text{Et})_2$, b. p. 257°—260°/50 mm., was obtained as a heavy, yellow oil by the action of

benzyl chloride on the sodium derivative of ethyl anilinomalonate. *Benzylanilinomalonate*, m. p. 170—173°, forms clusters of radiating needles; its *potassium* and *silver* salts are described. When the acid is heated above its m. p., it loses carbon dioxide and is converted into *α-anilino-β-phenylpropionic acid*, $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{NHPh})\cdot\text{CO}_2\text{H}$, m. p. 170—173°, which crystallises in lustrous plates. This acid, however, is most conveniently prepared by boiling an alcoholic solution of the benzylanilinomalonate acid; its *ethyl ester*, b. p. 206—209°/12 mm. or 218—221°/19 mm., m. p. 48—49°, forms stout, hexagonal prisms.

When *α-anilino-β-phenylpropionic acid* is heated with phenylthiocarbimide, *2-thio-4-benzyl-1:3-diphenylhydantoin*,



m. p. 129—130°, is produced which forms needle-like prisms, together with a small quantity of *α-benzylindoxyl*, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagdown \quad \diagup \\ \text{NH} \end{array} \text{CH}\cdot\text{CH}_2\text{Ph}$,

m. p. 271—272°, which crystallises in cubical prisms.

4-Benzyl-1:3-diphenylhydantoin, $\text{NPh} \begin{array}{c} \text{CO}\cdot\text{NPh} \\ \diagdown \quad \diagup \\ \text{CO}\cdot\text{CH}\cdot\text{CH}_2\text{Ph} \end{array}$, m. p. 58—62°,

is produced, together with a small amount of *α-benzylindoxyl*, by the action of phenylcarbimide on *α-anilino-β-phenylpropionic acid*; it can also be obtained by desulphurising *2-thio-4-benzyl-1:3-diphenylhydantoin*.

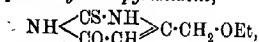
2-Thio-5-benzyl-7-phenyluramil, $\text{CS} \begin{array}{c} \text{NH}\cdot\text{CO} \\ \diagdown \quad \diagup \\ \text{NH}\cdot\text{CO} \end{array} \text{C}(\text{NHPh})\cdot\text{CH}_2\text{Ph}$,

m. p. 219—220°, obtained by treating an alcoholic solution of thiocarbamide with sodium ethoxide and ethyl benzylanilinomalonate crystallises in stout, prismatic blocks.

E. G.

Pyrimidines. LXXI. Synthesis of the Pyrimidine Nucleoside, *4-Hydroxymethyluracil*. TREAT B. JOHNSON and LEWIS H. CHERNOFF (*J. Amer. Chem. Soc.*, 1914, 36, 1742—1747).—In continuation of work on the nucleosides, *4-hydroxymethyltetrahydropyrimidin-2:6-dione* (*4-hydroxymethyluracil*) has been prepared by a method analogous to that used for the preparation of its 5-methyl derivative (A., 1913, i, 656).

When ethyl *γ*-ethoxyacetoacetate (Johnson, A., 1913, i, 588) is condensed with thiocarbamide in presence of sodium ethoxide, *2-thio-4-ethoxymethyltetrahydro-6-pyrimidone*,

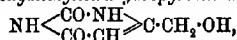


m. p. 180—181°, is obtained which crystallises in large, radiating prisms. On boiling this substance with chloroacetic acid in aqueous solution, it is converted into *4-ethoxymethyltetrahydropyrimidin-2:6-dione*,



m. p. 175°, which forms rhombic prisms; the latter compound is not changed by the action of 10% sulphuric acid at 140°, but when heated with concentrated hydrochloric acid at 100° it is converted into

4-chloromethyltetrahydropyrimid-2:6-dione, $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{CO} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{CH}_2\text{Cl}$,
 which crystallises in small, radiating prisms and decomposes at about
 214—215°. 4-Hydroxymethyltetrahydropyrimid-2:6-dione,



prepared by treating an aqueous solution of the chloropyrimidine successively with silver sulphate, hydrogen sulphide, barium hydroxide, and carbon dioxide, crystallises in small plates; it begins to melt at about 240°, decomposes at about 254°, and is readily reduced by hydriodic acid in presence of a little red phosphorus with formation of 4-methyluracil.

E. G.

Preparation of Acid Triphenylmethane Colouring Matters. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 269214).—Sulphonic acids of alkyl or arylalkyl derivatives of *m*-toluidines or mixtures of them are condensed with aromatic aldehydes containing no alkylamino-group in the para-position to the carbonyl group and the leuco-compounds thus obtained oxidised, or the amines are first condensed with the aldehydes and then sulphonated and oxidised. The acid triphenylmethane colouring matters formed in this way are mostly yellowish-green, and are faster than those prepared in a similar manner from aniline.

T. H. P.

Colour and Ionisation of Crystal-violet. ELLIOT Q. ADAMS and LUDWIG ROSENSTEIN (*J. Amer. Chem. Soc.*, 1914, 36, 1452—1473).—The rate of the development of colour when alkaline solutions of triphenylmethane dyes are acidified has been studied by Biddle (this vol., ii, 115), who calls attention to the complexity of the equilibrium in the case of crystal-violet as a result of the possibility of the formation of mono-, di-, and tri-acid salts. The colour changes produced by the gradual addition of mineral acid to an aqueous solution of a triphenylmethane dye (methyl-violet, crystal-violet, rosaniline, pararosaniline, malachite-green, and aniline-blue) are well-known. The authors observe that these changes in hue are accompanied by another change when the solutions are kept; the intensity of the colour diminishes greatly in strongly acidic or in alkaline solution (only in this case is the substance colloidal), and slowly in weakly acidic solution. Equivalent solutions of all strong acids produce identical effects, and on neutralisation the original colour is in every case restored, in hue at once, and in intensity by keeping. Evidently these changes are produced by reactions, which are completely reversible, of the chromogens with hydrogen or hydroxyl ions (or with water).

The phenomena, which have been fully examined in the case of crystal-violet as admitting of the greatest variety of salt-formation, necessitate two series of measurements, one dealing with the relative proportions of the differently coloured substances in the solution, the other with the variation of the proportions of the colourless substances with the colour of the solution.

The equilibrium between the differently coloured forms of crystal-violet has been examined by means of the spectrophotometer. The

absorption spectra of acidified solutions of the dye indicate that three substances, respectively, violet, green, and yellow, produce the colours of all the solutions. This assumption is substantiated by the fact that the absorption of solutions determined experimentally agrees with the absorption calculated by means of the molecular extinction coefficients; the completeness of the agreement establishes that three absorbing substances are necessary and sufficient to produce the observed absorption of all the solutions. By reasoning based on the fact that the colour of strong electrolytes is almost completely independent of the degree of ionisation, the inference is drawn that the violet, green, and yellow substances (in hydrochloric acid) are $C_{25}H_{30}N_3Cl$, $C_{25}H_{30}N_3Cl \cdot HCl$, and $C_{25}H_{30}N_3Cl \cdot 2HCl$ (or the positive ions produced therefrom) respectively.

The slow changes in colour intensity mentioned above occur at a rate and to an extent which increase with increasing acid concentration. With acid concentrations less than $N/10,000$ no measurable fading occurs, while in N -acid the colour almost disappears in the course of an hour. The reactions involved are unimolecular in both directions and are greatly influenced by temperature. The reactions which produce colourless from coloured modifications of the chromogen all occur in solutions extremely dilute with respect to chromogen. On the assumption that the only concentrations which can be changed appreciably are those of the coloured and colourless substances, an equation of a unimolecular reaction is developed and combined with a second equation involving the molecular extinction coefficient, whereby an expression is obtained from which are calculated data supporting the authors' contention that in strongly acidic solutions the principal colourless substance present is the carbinol ion produced by the dissociation of the carbinol trihydrochloride, $OH \cdot C(C_6H_4 \cdot NMe_2 \cdot HCl)_3$; in slightly acidic solutions the concentration of the carbinol ion derived from $OH \cdot C(C_6H_4 \cdot NMe_2)(C_6H_4 \cdot NMe_2 \cdot HCl)_2$ constitutes the largest part of the total carbinol concentration.

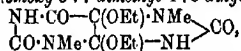
C. S.

Derivatives of 3:7-Dimethyluric Acid. HEINRICH BILTZ and PAUL DAMM (*Annalen*, 1914, 406, 22—59).—3:7-Dimethyluric acid can now be easily obtained from theobromine in more than 50% yield by chlorinating a very finely powdered suspension in chloroform and heating the resulting 8-chlorotheobromine (70—80% yield) with N -potassium hydroxide (1 mol.) on the water-bath.

5-Chloro-3:7-dimethyl- $\Delta^{4:9}$ -isouric acid, $\begin{matrix} NH \cdot CO - CCl \cdot NMe_2 \\ CO \cdot NMe_2 \cdot C \equiv N \end{matrix} > CO, m. p.$

about 168—169° (decomp.), is obtained by vigorously chlorinating 3:7-dimethyluric acid suspended in chloroform, the excess of chlorine being removed by a current of dry air. The substance can be prepared more conveniently, although not in so pure a state, by directing chlorinating theobromine in glacial acetic acid. It deliquesces in moist air, crystallises with difficulty, and is reduced to 3:7-dimethyluric acid by stannous chloride and hydrochloric acid. It liberates iodine from concentrated aqueous potassium iodide, but after solution in water is not affected by this salt, since it reacts with water to form 3:7-dimethyluric acid-4:5-glycol.

5-Chloro-3:7-dimethylisouric acid (prepared by the second method and therefore containing $C_5H_4O_2$) reacts with anhydrous ethyl alcohol at 0° to form 4:5-diethoxy-3:7-dimethyl-4:5-dihydrouic acid,



m. p. $220-221^\circ$ (decomp.), white, crystalline powder; the corresponding dimethoxy-compound sinters at about 195° and has m. p. $216-217^\circ$ (decomp.). The ethers are reduced to 3:7-dimethyluric acid by sodium amalgam or hydriodic acid, D 1.96.

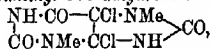
5-Chloro-3:7-dimethylisouric acid is converted by a mixture of alcohol and pyridine at 0° into 5-ethoxy-3:7-dimethylisouric acid, m. p. 191° (decomp.), rectangular plates; the corresponding methoxy-derivative has m. p. $205-206^\circ$. The ethoxy-derivative reacts with alcoholic hydrogen chloride or with concentrated hydrochloric acid to form respectively 4:5-diethoxy-3:7-dimethyl-4:5-dihydrouic acid or the semi-ether mentioned below.

4-Hydroxy-5-ethoxy-3:7-dimethyl-4:5-dihydrouic acid, m. p. $228-229^\circ$, sintering at 215° , has been prepared in several ways: (i) by the action of concentrated hydrochloric or sulphuric acid on 4:5-diethoxy-3:7-dimethyl-4:5-dihydrouic acid; (ii) by the chlorination of 3:7-dimethyluric acid in anhydrous alcohol; (iii) by the chlorination of the bromine in a cooled mixture of alcohol and chloroform; (iv) by heating to boiling an alcoholic solution of 5-chloro-3:7-dimethylisouric acid containing a few drops of concentrated hydrochloric acid (best method). The substance is extraordinarily stable, being unattacked by concentrated sulphuric acid at room temperature, boiling glacial acetic acid and hydrogen chloride, potassium chlorate and hydrochloric acid, water at 170° , or boiling 2*N*-sodium hydroxide. It yields 1-methylhydantoin by reduction with hydriodic acid (D 1.46), methylparabanic acid by oxidation with nitric acid (D 1.5), on the water-bath, and 3:7-dimethyluric acid-4:5-glycol by heating with concentrated sulphuric acid at $80-90^\circ$ and subsequent treatment with water. The preceding behaviour and the methods of preparation afford satisfactory proof of the constitution of 4-hydroxy-5-ethoxy-3:7-dimethyl-4:5-dihydrouic acid. Attempts to convert it into the diethoxy-derivative have been unsuccessful; however, it yields an acetyl compound, $C_{11}H_{10}O_6N_2$, m. p. 165° , hexagonal plates.

4-Hydroxy-5-methoxy-3:7-dimethyl-4:5-dihydrouic acid, m. p. $247-248^\circ$, stout rhombohedra, is prepared by the same methods as the ethoxy-compound and resembles it in behaviour and properties.

4-Hydroxy-5-propoxy-3:7-dimethyl-4:5-dihydrouic acid, m. p. $203-204^\circ$ (slight decomp.), leaflets, is obtained by boiling 5-chloro-3:7-dimethylisouric acid with propyl alcohol.

4:5-Dichloro-3:7-dimethyl-4:5-dihydrouic acid,



flattened needles or elongated leaflets containing $C_5H_4O_2$, sintering at about 150° , and carbonising above 300° , is obtained by vigorously chlorinating 3:7-dimethyluric acid in glacial acetic acid at 0° , and closely resembles 5-chloro-3:7-dimethylisouric acid in its properties

and behaviour. When 3:7-dimethyluric acid is chlorinated at 0° in glacial acetic acid containing water (1 mol.), the product is 5-chloro-4-hydroxy-3:7-dimethyl-4:5-dihydrouic acid, stout prisms containing $C_8H_8O_8$, sintering below 100°, and m. p. 180°, which does not exhibit the murexide reaction, and therefore is not a derivative of ψ -uric acid. The substance is converted into 3:7-dimethyluric acid:4:5-glycol by water, into 4-hydroxy-5-ethoxy-3:7-dimethyl-4:5-dihydrouic acid by alcohol and into 4-hydroxy-3:7-dimethyl-4:5-dihydrouic acid by a saturated solution of hydrogen iodide in glacial acetic acid. The last substance is stable to alkalis and to concentrated sulphuric acid at room temperature, and cannot be converted into 3:7-dimethyluric acid by dehydrating agents. Its constitution is deduced from the following reactions. It forms an ammonium salt, m. p. 174—175° (decomp.), slender needles, yields 5-chloro-4-hydroxy-3:7-dimethyl-4:5-dihydrouic acid, 4-hydroxy-5-ethoxy-3:7-dimethyl-4:5-dihydrouic acid, and 3:7-dimethyluric acid:4:5-glycol by chlorination in glacial acetic acid, alcohol, and water respectively, and is converted into 1-methylhydantoin by fission with boiling hydrochloric acid. The last transformation is important, since it proves that the hydroxyl group is in position 4, not 5. C. S.

Derivatives of 4:5-Dialkyloxy-3:7-dimethyl-4:5-dihydrouic Acid. HEINRICH BILTZ and PAUL DAMM (*Annalen*, 1914, 406 59—100).—Only about 50% of the theoretical yield of 4-hydroxy-5-ethoxy-3:7-dimethyl-4:5-dihydrouic acid is obtained by chlorinating theobromine in alcoholic solution (preceding abstract). By the addition of ether to the concentrated mother-liquor, a substance, $C_{19}H_{15}O_8N_3$, is ultimately obtained, the origin of which is explained below.

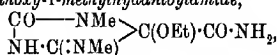
By heating 4:5-diethoxy-3:7-dimethyl-4:5-dihydrouic acid with alcoholic hydrogen chloride on the water-bath until solution is complete, and subsequently adding ether, the hydrochloride, $C_{17}H_{13}O_8N_4.HCl$, m. p. 191—192° (decomp.), leaflets, of a substance is obtained, which proves to be ethyl 4-methylimino-5-ethoxy-1-methylhydantoylcarbamate, $\begin{matrix} \text{CO—NMe} \\ | \\ \text{NH}\cdot\text{C}(\text{NMe}) \end{matrix} > \text{C(OMe)}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, m. p. 204—205°, quadratic prisms. The hydrochloride, which can also be prepared by the chlorination of theobromine or 3:7-dimethyluric acid under suitable conditions, loses hydrogen chloride by treatment with water or cold aqueous-sodium hydroxide, and yields 3:7-dimethyluric acid by reduction with sodium an amalgam. The latter transformation, by suggesting that the hydrochloride is a near relative of 3:7-dimethyluric acid, misled the authors as to the constitution of the carbamate until the discovery was made that hydrochlorides of mixed dialkyloxy-derivatives can be prepared. Thus the hydrochloride, m. p. 190—191° (decomp.), of methyl 4-methylimino-5-ethoxy-1-methylhydantoylcarbamate, m. p. 210—211°, elongated prisms, is obtained from 4:5-diethoxy-3:7-dimethyl-4:5-dihydrouic acid and methyl-alcoholic hydrogen chloride. In a similar manner have been obtained the hydrochloride, m. p. 204—205° (decomp.), of methyl 4-methylimino-5-methoxy-1-methyl-

hydantoylcarbamate, m. p. 188—189°, needles or prisms (*acetyl* derivative, m. p. 184—185°, stout rhombohedra), and the *hydrochloride*, m. p. 179—180° (decomp.), of *ethyl 4-methylimino-5-methoxy-1-methylhydantoylcarbamate*, m. p. 198—199°, long needles.

By boiling with water or dilute hydrochloric acid, the preceding carbamates (in the form of their hydrochlorides) exchange the methylimino-group in position 4 for oxygen. Thus *ethyl 4-methylimino-5-ethoxy-1-methylhydantoylcarbamate hydrochloride* gives a quantitative yield of methylamine hydrochloride, the other product (the substance, $C_{10}H_{18}O_6N_2$, mentioned above) being *ethyl 5-ethoxy-1-methylhydantoylcarbamate*, $\begin{matrix} \text{CO} \cdot \text{NMe} \\ | \\ \text{NH} - \text{CO} \end{matrix} > \text{C}(\text{OEt}) \cdot \text{CO} \cdot \text{NH} \cdot \text{CO}_2\text{Et}$, m. p. 170°, stout plates,

which yields methylparabanic acid by oxidation and 1-methylhydantoin by reduction with hydriodic acid, D 1.96, at about 80°. *Methyl 5-methoxy-1-methylhydantoylcarbamate*, m. p. 110—120° (hydrated) or about 177—178° (anhydrous), prisms containing H_2O or rhombic leaflets (*acetyl* derivative, m. p. 165—166°, stout rhombohedra), *methyl 5-ethoxy-1-methylhydantoylcarbamate*, m. p. 186—187°, stout, double pyramids, and *ethyl 5-methoxy-1-methylhydantoylcarbamate*, m. p. 170—171°, stout crystals, are obtained in a similar manner.

Ethyl 4-methylimino-5-ethoxy-1-methylhydantoylcarbamate and the other three substances of the same type are attacked by alcoholic ammonia at the carbethoxy-group, ethyl alcohol and carbon dioxide being eliminated and a hydantoylamide being produced. Thus *ethyl* and *methyl 4-methylimino-5-ethoxy-1-methylhydantoylcarbamates* yield *4-methylimino-5-ethoxy-1-methylhydantoylamide*,



m. p. 240—241° (decomp.), leaflets or plates, while *methyl* and *ethyl 4-methylimino-5-methoxy-1-methylhydantoylcarbamates*, in the form of their hydrochlorides, yield *4-methylimino-5-methoxy-1-methylhydantoylamide*, m. p. 254—255° (decomp.), clusters of elongated prisms. These two hydantoylamides retain their methylimino-group even when they are boiled with concentrated aqueous ammonia or kept with dilute hydrochloric acid for many days; by heating with concentrated hydrochloric acid, however, they undergo extensive decomposition. Solutions of the amides in dilute sodium hydroxide, prepared at room temperature, exhibit an intense biuret reaction. *4-Methylimino-5-methoxy-1-methylhydantoylamide* does not form a silver salt or react with methyl sulphate and sodium hydroxide, but is readily acetylated by boiling acetic anhydride, forming the *acetyl* derivative, sintering at 173°, decomp. 184°, long rhombohedra, which can be crystallised from boiling water.

Ethyl and *methyl 5-ethoxy-1-methylhydantoylcarbamates* are converted by evaporation with concentrated aqueous ammonia into *5-ethoxy-1-methylhydantoylamide*, $\begin{matrix} \text{CO} \cdot \text{NMe} \\ | \\ \text{NH} - \text{CO} \end{matrix} > \text{C}(\text{OEt}) \cdot \text{CO} \cdot \text{NH}_2$, m. p. 206—207°, elongated rhombohedra or rhombic leaflets; *5-methoxy-1-methylhydantoylamide*, obtained in a similar manner from *ethyl* and *methyl 5-methoxy-1-methylhydantoylcarbamates*, has m. p. 225°, and

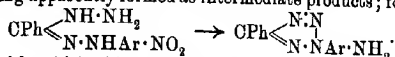
forms an *acetyl* derivative, sintering at about 85° , m. p. 110° , by prolonged boiling with acetic anhydride. The ethoxy- and methoxy-methylhydantoylamides are identical with the products obtained by the ethylation and methylation respectively of 5-hydroxy-1-methylhydantoylamide.

Hypocaffeine is obtained readily and in good yield by passing hydrogen chloride through a fused mixture of *s*-dimethylcarbamide and 5-hydroxy-1-methylhydantoylamide.

5-Ethoxy-1:3-dimethylhydantoylamide is obtained by treating 5-ethoxy-1-methylhydantoylamide with methyl sulphate and 2*N*-sodium hydroxide; 5-methoxy-1:3-dimethylhydantoylamide, prepared in a similar manner, has m. p. 198° . Ethyl 5-ethoxy-1:3-dimethylhydantoyl-carbamate, m. p. 134° , and methyl 5-methoxy-1:3-dimethylhydantoyl-carbamate, m. p. $161-162^{\circ}$, prepared by the methylation of the respective monomethyl compounds, are converted into 5-ethoxy- and 5-methoxy-1:3-dimethylhydantoylamides respectively by concentrated aqueous ammonia on the water-bath.

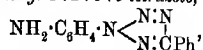
C. S.

New Method of Preparation of Tetrazoles. G. Ponzio and C. MACCIOTTA (*Gazzetta*, 1914, **44**, ii, 63-72).—The action of hydrazine hydrates on nitro-substituted arylhydrazones of ω -nitrobenzaldehyde yields amino-derivatives of substituted 1:2:3:5-tetrazoles, hydrazonohydrazides being apparently formed as intermediate products; for instance,



The ease with which this reaction occurs renders it useful for the preparation of tetrazoles unobtainable in other ways. The reaction is to some extent analogous to Dimroth and Merzbacher's synthesis of tetrazoles (*A.*, 1910, i, 897).

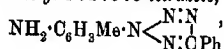
4-Phenyl-1-*p*-aminophenyl-1:2:3:5-tetrazole,



prepared from ω -nitrobenzaldehyde-*p*-nitrophenylhydrazone, forms small, white prisms or long needles, m. p. 164° , turning yellow in the air. Like the other tetrazole derivatives described below, it gives with mineral acids well crystallised salts, which undergo hydrolysis with greater or less ease. The *sulphate*, $(\text{C}_{13}\text{H}_{11}\text{N}_5)_2\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$, decomposing at about 215° , the *nitrate*, $\text{C}_{13}\text{H}_{11}\text{N}_5\cdot\text{HNO}_3$, turning brown at about 180° and decomposing at about 200° , and the *hydrochloride*, $\text{C}_{13}\text{H}_{11}\text{N}_5\cdot\text{HCl}$, turning brown at 200° , m. p. 210° (decomp.), were prepared. When the diazo-derivative of the sulphate is heated with alcohol, 1:4-diphenyl-1:2:3:5-tetrazole (compare Forster and Cardwell, *T.*, 1913, **103**, 870) is obtained.

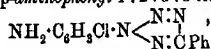
4-Phenyl-1-*o*-aminophenyl-1:2:3:5-tetrazole, $\text{C}_{13}\text{H}_{11}\text{N}_5$, prepared from ω -nitrobenzaldehyde-*o*-nitrophenylhydrazone, forms flattened, yellow needles, m. p. 80° .

4-Phenyl-1-*p*-amino-*o*-tolyl-1:2:3:5-tetrazole,



prepared from ω -nitrobenzaldehyde-*p*-nitro-*o*-tolylhydrazones, forms white prisms, m. p. 121°, rapidly turning yellow in the air.

4-Phenyl-1-*o*-chloro-*p*-aminophenyl-1:2:3:5-tetrazole,



prepared from ω -nitrobenzaldehyde-*o*-chloro-*p*-nitrophenylhydrazones, forms shining, flattened needles, m. p. 134°.

T. H. P.

The Adsorption of Electrolytes and Colloids by Casein. HERMAN PALME (*Zeitsch. physiol. Chem.*, 1914, 92, 177—193).—The author has shaken casein with solutions of ferrocyanic acid, copper acetate, colloidal ferric oxide, and ferric chloride, and has determined the influence of concentration on the amount of material adsorbed by the casein. With the first two substances, the amount adsorbed varied with their concentration in accordance with the formulæ put forward by Arrhenius, Freundlich and Schmidt. In the case of the iron compounds it was found that the amount of iron adsorbed depended on the total quantity of electrolyte in the solution.

H. W. B.

Mykommucin. ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1914, 92, 144—148).—The mucin was obtained from a tumour by extraction with water and subsequent precipitation with acetic acid. The product after reprecipitation contained C 50.82%, H 7.27%, N 12.24%, S 1.19%, and P 0.25%; and gave positive biuret, Millon's, xantho protein, Molisch's and Ehrlich's dimethylaminobenzaldehyde reactions. The solution in alkali was precipitated by dilute acid and the precipitate was not soluble in excess of the acid. It contained at least 12% of a carbohydrate which was split off on hydrolysis with a dilute mineral acid and, from the crystalline form and general properties of its hydrochloride, was recognised as glucosamine. The new mucin differs, in certain particulars, from all known mucins.

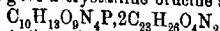
H. W. B.

The "Carbohydrate" Group of the True Nucleic Acids. R. FEULGEN (*Zeitsch. physiol. Chem.*, 1914, 92, 154—158).—The author draws the conclusion, from a study of the properties of thymic acid, derived from thymonucleic acid, that the so-called carbohydrate group of the nucleic acids is in reality glucal or a similar substance (compare E. Fischer, this vol., i, 252). The reasons for this conclusion are (i) the ease with which the compound is destroyed by dilute mineral acids or alkalis; (ii) the production of a green pine-wood splinter reaction, and (iii) the rapid appearance of an intense reddish-violet coloration with Schiff's reagent. Further, the figures obtained on elementary analysis of nucleic acid agree more closely with the theory on the assumption of glucal instead of hexose groups in the molecule.

H. W. B.

Oxidation of Guanylic Acid to "Xanthylic Acid" by Means of Nitrous Acid. MARTIN KNOPF (*Zeitsch. physiol. Chem.*, 1914, 92, 159—162).—Sodium guanylate was treated in aqueous solution with sodium nitrite and acetic acid, and the resulting

xanthylic acid precipitated by the addition of excess of alcohol. The acid after purification gave a crystalline brucine salt,



(needles from 30% alcohol), which began to melt at 200° . Hydrolysis of the raw product gave only xanthine, the absence of guanine showing that the guanylic acid had been completely de-amidised.

H. W. B.

Action of Some Diastases on the Dextrins. (Mme.) Z. GAUZEWSKA (*Compt. rend.*, 1914, 159, 343—345).—A comparison of the influence of amylases of animal and vegetable origin on the erythro-dextrin obtained from starch and the achroodextrin from glycogen by the action of hydrogen peroxide. In the case of the amylase in the pancreatic juice of the dog, vegetable amylase, taka-diastase, and the juice of the snail, the ratio between the amounts of sugar obtained from the two dextrins is practically identical with the ratio between the amounts of sugar obtained from starch and glycogen under similar conditions.

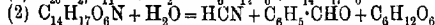
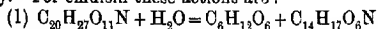
W. G.

Influence of the Reaction of the Medium on the Action of the Inulase of *Aspergillus niger*. A. KIRSSEL (*Ann. Inst. Pasteur*, 1914, 28, 747—757).—Whilst all the acids employed increased the activity of the diastase, a difference was observed between acetic acid and mineral acids. With acetic acid the activation obtained by the neutralisation (to helianthin) of the diastatic solution was changed very slightly up to the point at which the activity was diminished. With mineral acids, the activity increased regularly as the acidity increased. In the case of phosphoric acid the maximum activation was within the limits between 1/90 and 1/72 mol. gram; with acetic acid between 1/2000 and 1/50 mol. gram.

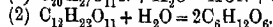
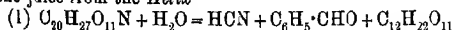
It was to be expected that as the activity of inulase is increased by acids, it would be increased by acid salts still further than by neutral salts. Experiments with hydrogen sodium citrate and disodium citrate showed, however, a reversed effect, the increase obtained with the two salts being respectively 19 and 104%. With dihydrogen sodium phosphate the increase was 131%.

N. H. J. M.

Coupled Enzyme Actions. J. GHAJA (*Compt. rend.*, 1914, 159, 274—276).—The hydrolysis of amygdalin by the emulsin of almonds and by the digestive juice of *Helix pomatia* must be considered as the product of two conjoined enzyme actions, the one primary and the other secondary. For emulsin these actions are:



and for the juice from the *Helix*:



For emulsin the velocity of production of reducing sugar increases with the concentration of the amygdalin, whilst the velocity of formation of hydrogen cyanide is greater the lower the concentration of

the amygdalin. For the juice of the *Helix*, the velocity of formation of hydrogen cyanide is independent of the concentration of the amygdalin, whilst the velocity of production of reducing sugar increases as the concentration of amygdalin decreases. In each case a low concentration of amygdalin favours the secondary enzyme action.

W. G.

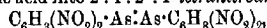
Action of Chymosin [Rennet] and Pepsin. I. The Clotting-velocity as a Measure of the Amount of Chymosin Present. OLOF HAMMARSTEN (*Zeitsch. physiol. Chem.*, 1914, 92, 119—143).—The author finds that the so-called Time-Law (amount of chymosin \times clotting-time = constant), which holds good at 37—40°, is not obeyed at lower temperatures. At 20°, the chymosin may be much more active than at 40°, and the product correspondingly too large. The observations were carried out with acid and with neutral and dialysed extracts of stomach, with similar results in every case.

The effect of dilution varies, but usually increases the activity of the enzyme. It is suggested that by dilution inactive enzyme may become active by a process of dissociation.

H. W. B.

Aromatic Arsenic Compounds. VIII. Some New Reduction Products of 2:4-Dinitrophenylarsinic Acid and a Large Class of New Carbamic Acid Derivatives. P. KARRER (*Ber.*, 1914, 47, 2275—2283. Compare this vol., i, 890, 891).—By treating an ethereal solution of 2:4-dinitrophenylarsinic acid with phosphorus trichloride and water successively (compare Ehrlich and Berthelm, A., 1910, i, 451) reduction is effected to 2:4-dinitrophenylarsenoxide, $C_6H_3(NO_2)_2 \cdot AsO$, a yellow, crystalline solid which is almost insoluble in dilute mineral acids and the common organic solvents, but dissolves in ether or alcohol containing hydrogen chloride, giving dinitrophenylarsenic dichloride and in excess of aqueous sodium hydroxide to a yellow solution. When exposed to sunlight an ethereal solution of the arsenoxide gave an almost black, crystalline deposit of uncertain nature (compare Karrer, this vol., i, 891).

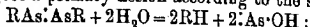
Reduction of hypophosphorous acid in aqueous solution at 50—60°, in the presence of a little potassium iodide as catalyst, converts 2:4-dinitrophenylarsinic acid into 2:4:2':4'-tetranitroarsenobenzene,



which separates in reddish-brown flocks. This substance is easily oxidisable and is very sparingly soluble in all solvents.

A solution of stannous chloride in hydrochloric acid at 70—80°, on the other hand, reduces dinitrophenylarsinic acid to 2:4:2':4'-tetraaminoarsenobenzene, $C_6H_3(NH_2)_4 \cdot As:As \cdot C_6H_3(NH_2)_4$, which, on pouring the reaction product into acetic acid, separates in yellowish-white flocks of the zincchloride. The free base was obtained by dissolving the zincchloride in 2- to 3-N-hydrochloric acid and then adding successively acetic acid and ether, when the base separated as a yellowish-white precipitate. Both the base and the zincchloride are unstable in aqueous solution, rapidly giving a deep reddish-brown precipitate similar to those produced more slowly from solutions of

many organic arsenic compounds on keeping (compare Ehrlich and Berthelm, A., 1912, 1, 523), although they are stable in solution in concentrated hydrochloric acid. As, after the decomposition in aqueous solution, the filtrate from the red precipitate is found to contain arsenic and arsenious acids, together with *m*-phenylenediamine, it is believed that the decomposition is a hydrolytic one, in which the molecule undergoes a primary fission according to the scheme



approximately one-quarter of the tetra-aminoarsenobenzene is found to pass into *m*-phenylenediamine, whilst the remainder gives the insoluble brown substance. Although in the dry condition, even in an exhausted space, tetra-aminoarsenobenzene undergoes complete decomposition within forty-eight hours, the base can be coupled in the usual manner of meta-diamines with diazo-compounds, yielding azo-dyes containing arsenic, and when itself diazotised, it gives a precipitate of a reddish-brown substance, probably of the Bismarck-brown type.

A remarkable property of 2:4:2':4'-tetra-aminoarsenobenzene is that its solution in dilute hydrochloric acid when treated with sodium carbonate or hydrogen carbonate gives a precipitate of the base which is soluble in excess, although the resulting solution is unstable, and shortly deposits a flocculent solid. 3:5:3':5'-Tetra-amino-4:4'-dimethylaminoarsenobenzene has already been observed to exhibit similar behaviour (Giemsa, *Munch. Med. Woch.*, 1913, 1074), which is believed to depend on the formation of a carbamic acid derivative. The conclusion is drawn that this solubility in sodium hydrogen carbonate is to be attributed to the amino-groups in the meta-position, and examination reveals the fact that *m*-diamines generally, whether containing arsenic or not, are soluble in sodium carbonate or hydrogen carbonate solution in the presence of free carbon dioxide. This reaction is therefore of great value for the characterisation of meta-diamines, as ortho- and para-diamines do not exhibit this behaviour. That the solutions produced actually contain carbamic acid derivatives and not carbonates of the respective bases is shown by the absence of precipitation on the addition of sodium hydroxide. The solutions of the various carbamic acid compounds vary widely in stability, ranging from that derived from the above-mentioned tetra-aminodimethylaminoarsenobenzene which is very stable to that from 2:4:2':4'-tetra-aminoarsenobenzene which decomposes in a few seconds.

D. F. T.

Preparation of a 3:5:3':5'-Tetra-amino-4:4'-dimethylamino-



arsenobenzene. C. F. BOEHRINGER & SÖHNE (Swiss Patent, 64347).—This compound (annexed formula), m. p. 95° (decomp.),

is prepared from an arseno-benzene derivative containing, in the para-position to the arsenical radicle, the group $NRMe$, where R represents either a hydrogen atom, or a methyl group, or an acyl radicle; this is treated with a mixture of nitric and concentrated sulphuric acids, and the 3:5-diamino-4-methylnitroaminobenzene-1-arsinic acid thus

obtained is reduced in acid solution. The base has valuable therapeutic properties, as it exerts a pronounced action on trypanosomes and similar disease-producers, whilst its toxic effect on the human organism is less marked than that of other arsenic compounds. The hydrochloride, $C_{14}H_{20}N_9As_2 \cdot 4HCl$, is a yellowish-green powder and dissolves very readily in water.

T. H. P.

Physiological Chemistry.

The Influence of the Oxygen Content of the Surrounding Medium on the Gaseous Metabolism and the Rate of Oxidation in the Frog. ERNST J. LESSER (*Biochem. Zeitsch.*, 1914, 65, 400—408).—In a series of experiments of twenty-two hours' duration on consecutive days, it was found that the respiratory quotient remained practically constant, although there were variations (10—20%) in the amount of oxygen used (rate of oxidation). The amount of oxygen consumed by the same frogs was found to remain the same, when the oxygen of the atmosphere was reduced, until the amount fell to below about 2.8%. The diminution of the oxygen tension is accompanied, however, with a rise in the respiratory quotient. The author explains these phenomena by assuming that the oxygen pressure in the cells is diminished, and this causes an increased rate of hydrolysis of glycogen. Sugar is thus mobilised and burnt. The rate of hydrolysis by glycogen is not due thus to the rate of oxidation of the organism, but to the oxygen tension in the cell.

S. B. S.

Substance Hitherto Unknown in Human and Some Animal Serums. W. FRIEBOES (*Chem. Zentr.*, 1914, i, 2007; from *Deut. Med. Woch.*, 1914, No. 12).—The substance is very similar to the acid saponins; it reduces gold chloride, reacts with Nessler solution, and is precipitated by neutral lead acetate. It is rendered non-poisonous by cholesterol, and less poisonous by bromine and baryta. The name "saponoid" is suggested.

N. H. J. M.

The "Specific-dynamic Action" of Foodstuffs. S. CSERNA and G. KELEMEN (*Biochem. Zeitsch.*, 1914, 66, 63—74).—The intravenous injection of various substances, such as sodium chloride, dextrose, or carbamide increases the gaseous exchanges of eviscerated animals (dogs). This action of various substances on gaseous exchange cannot be due, therefore, as Zuntz has suggested, to increased work of secretion by the alimentary tract, or to increased work of the kidneys. The substances must act, as Tangl has thought, by a general stimulation of the cells, which increases their metabolism of energy and matter.

S. B. S.

The Behaviour of Amino-acids in the Metabolism of Birds. K. SZALÁGYI and A. KRIWUSCHNA (*Biochem. Zeitsch.*, 1914, 66, 139—148).—The methods of determining the amino-acids by van Slyke's method in the urine and faeces of birds are described. The urine was collected from fistulae. To a basal diet of maize was added asparagine, glycine, and molasses with known amino-acid content. All the asparagine was absorbed, as indicated by the amino-acid content of the faeces, when the animals were on the basal diet, and on this diet + the amino-acid. This was not the case with either glycine and molasses, as the addition of these to the basal diet caused an increase of amino-acids in faeces (3.76—9.03%). The increased amount of amino-acids in the urine varied between 2.83 and 6.90% of the amino-acids absorbed, the smallest numbers being obtained with asparagine.

S. B. S.

The Relationship Between the Energy Exchange and the Protein Metabolism During Starvation. PAUL HÄRT (*Biochem. Zeitsch.*, 1914, 66, 1—19).—The necessary energy required for maintenance of dogs at their critical temperatures (28°) during the first (second to eighth) days of starvation varies with different individuals between 700 and 1,000 cal. per square metre of body surface. The minimal amount is independent of the size of the animal, but depends on the amount of protein decomposed in the body. The increase of energy depends, not only on the larger amount of protein destroyed, but also on an increased combustion of the fat. This latter phenomenon appears to be due to some specific dynamic action of the decomposed proteins; the degradation products of the latter may perhaps exert some sort of chemical action on the fats, so as to render them liable to combustion.

S. B. S.

The Energy Exchange on Insufficient Diets. PAUL HÄRT (*Biochem. Zeitsch.*, 1914, 66, 20—47).—If a dog, after a short period of starvation, is fed daily with an amount of milk which is insufficient for its energy needs, the daily exchange in chemical energy during this period of chronic underfeeding is either slightly increased or else it shows a gradual apparent decline. It shows an increase in those animals which in the foregoing period of starvation and during the period of underfeeding undergo only a slight loss of proteins, whereas it shows a decline in those animals in which the loss in proteins is relatively high. The milk exerts a specific dynamic action, which can be demonstrated in those animals which have suffered a protein loss, and in which, therefore, the energy necessary for maintenance has diminished.

S. B. S.

The Permanent Intravenous Injection of Peptones and Proteins. V. HENRIQUES and A. C. ANDERSEN (*Zeitsch. physiol. Chem.*, 1914, 92, 194—211. Compare this vol., i, 107, 1029).—The author has found it possible to maintain goats alive for two and a-half days after the removal of their intestines. During this time the animals have retained a small amount of nitrogen when fed

by the author's method of permanent intravenous injections with the products of tryptic-ereptic digestion of meat. The agency of the intestinal cells is, therefore, apparently not essential for protein synthesis.

Attempts to maintain nitrogenous equilibrium in goats or calves by intravenous injections of Witte's peptone, casein, and egg-white were usually unsuccessful owing to the acute toxic action of these substances. A positive nitrogen balance was obtained by the injection of serum into a goat, a turkey, and a calf, but in most experiments symptoms of poisoning supervened, resulting in death.

H. W. B.

Estimations of Tryptophan in Normal and Pathological Kidneys. ELISABETH KURCHIN (*Biochem. Zeitsch.*, 1914, **65**, 451-459).—The estimation of tryptophan was made in human kidneys removed from a large number of cases in which the organs were normal and abnormal. The expressed juices and the residues were investigated separately, and were then digested for twenty-four hours with trypsin. The tryptophan in the digest was estimated by means of *p*-dimethylaminobenzaldehyde, the blue colour produced being compared with a standard ammoniacal copper solution according to Herzfeld's method. The tryptophan was found to be somewhat higher in normal than in pathological cases, and increases generally with the age of the individual. The lowest figures were found in a case of chronic interstitial nephritis.

S. B. S.

Extractives of Muscle. XVI. The Isolation of Carnosine by means of Mercuric Sulphate. M. DIETRICH (*Zeitsch. physiol. Chem.*, 1914, **92**, 212-213).—Carnosine is precipitated from the aqueous extract of muscle by mercuric sulphate dissolved in 5% sulphuric acid instead of by the more expensive phosphotungstic acid. The addition of two volumes of alcohol and a little ether just before the mercuric sulphate solution greatly increases the rapidity with which the carnosine is precipitated. By this method, 0.17% of crystalline carnosine was obtained from calf's muscle.

H. W. B.

The Occurrence of Carnosine, Methylguanidine, and Carnitine in Mutton. J. SMORODINZEV (*Zeitsch. physiol. Chem.*, 1914, **92**, 221-227. Compare this vol., ii, 759).—An extract of mutton was analysed by two methods: (1) precipitation of the bases directly with mercuric sulphate in sulphuric acid solution, followed by treatment of the filtrate after removal of the mercury with phosphotungstic acid; (2) treatment with lead acetate, and subsequent isolation of the bases with phosphotungstic acid. Method (1) gave, as in the case of the extract of beef (*loc. cit.*), more purine, carnosine, and carnitine, but less methylguanidine, than method (2). Expressing the results as percentages of the fresh muscle of the sheep, the amount of purine extracted was 0.058, carnosine 0.115, methylguanidine 0.038, carnitine 0.047, and

creatine 0.173. Extract of beef contains three times as much carnosine as extract of mutton.

H. W. B.

Preparation of Carnosine from the Broth Formed During the Sterilisation of Meat by Steam in the Hönnecke Meat-steamer. J. SMORODINZEV (*Zeitsch. physiol. Chem.*, 1914, 92, 228—230, Compare preceding abstract).—By means of the mercuric sulphate process, 22.4 grams of carnosine were obtained from 10.5 litres of broth. This represents about 0.064 gram of carnosine per 100 grams of ox muscle. It follows that during the process of sterilisation about three-fourths of the extractives are retained in the meat.

H. W. B.

The Influence of a Diet Poor in Calcium on the Composition of Growing Bones. STEPHAN WEISER (*Biochem. Zeitsch.*, 1914, 66, 95—114).—As a result of experiments on young pigs, it was found that a diet poor in calcium caused the increase of body-weight to be 20% less than in control animals fed on a diet with normal calcium content. If the calcium deprivation continued for a longer period, the animals commenced to lose weight. The appearance of the bones of the animals on a calcium-poor diet was also different. They were thinner, deformed, and easily cut with a knife. The growth and weight of the skeleton was not, however, smaller, but the bones were richer in water and poorer in calcium and ash-content when calcium was withheld. The amount of alkalis in the ash in the bones of animals on calcium-poor diet was larger than in the control animals, and they contained more sodium than potassium.

S. B. S.

The Action of Moderators (Buffers) in Altering the Acid-base Equilibrium in Biological Fluids. MAX KOPPEL and K. SPIRO (*Biochem. Zeitsch.* 1914, 65, 409—439).—A definition is given of the moderating (buffer) action of substances. The amount S of an acid added to a solution produces a certain change in the negative exponent of the hydron concentration p ($p = -\log[H]$). Suppose a given amount of acid ΔS_0 produces a change Δp in the absence of a moderator, and the same change is produced by an amount ΔS in the presence of the moderator. The moderating action P can then be indicated by the expression $\Delta(S - S_0)/\Delta p$. The following expression for the moderating action of a weak acid is then deduced from the laws of ionic mass reaction, $P = -Ak_x/(k_x + x)^2 \log 10$, where x = the hydron concentration, k_x = the dissociation constant of the acid, and A is the equivalent concentration in which it is present. From such an expression it is evident that the moderating action of an acid is proportional to the equivalent concentration in which it is present. Where x is very large (that is, in the case of strong acids) or very small (as in the case of strong bases), the value of P becomes, therefore, diminishingly small. The maximum is where the value $x = k_x$, that is to say, the buffer action of a monobasic acid exhibits its maximum when the hydron concentration is numerically equal to its dissociation constant. Just half of the acid is then present

as free acid and the other half as salt. All moderators, therefore, act efficiently for a certain value of p . In the above formula, if $x=k_s$, $P=-A/4 \log 10$. From this it follows that the maximal buffer action of all weak acids in the same equivalent concentration is the same, and is proportional to that concentration. For a normal acid $P=-\log 10/4$. It is not, therefore, correct to speak of strong or weak "buffers," apart from the concentration, as this buffer action depends only on the position of the substance in the series of p values.

Owing to the maintenance of a constant neutrality in the organism, just those acids will be effective as buffers the k_s value of which is near 10^{-7} (that is, the hydrion concentration of the neutral point). It is for this reason that phosphoric and carbonic acids act so effectively in the body fluids, etc.

Similar theoretical deductions have been made as to the buffer action of ampholytes. Here, three cases can be distinguished (k_b =the basic and k_s the acid dissociation constants of the ampholyte): (1) When $k_b \cdot k_s > k_w/16$. In this case there is only one point of maximal action of the moderator, viz., at the isoelectric point of the ampholyte. (2) When $k_b \cdot k_s < k_w/16$. In this case the moderating action is at a minimum at the isoelectric point of the ampholyte. There are in this case two points of maximal action, situated equidistantly from the isoelectric point, and of about the same magnitude. (3) The third case is when $k_b \cdot k_s = k_w/16$. This is of theoretical interest only.

The theoretical considerations have also been applied to the determination of the positions of maximal moderating actions in the case of substances with two or more dissociation stages (poly-basic acids, etc.).

The theoretical deductions are illustrated by curves showing the moderating action of acetic acid, glycine, and various urines, the $(S-S_0)$ values being plotted as the ordinates and the p values on the abscissæ.

S. B. S.

Does Normal Urine Contain Free Glycerol? MILAN FARNAS (*Biochem. Zeitsch.*, 1914, 66, 115—121).—A method is described for obtaining the glycerol by distillation in steam in a vacuum of the liquid under investigation, the apparatus used for this purpose being figured and described. The glycerol in the distillate was then estimated by the Zeisel-Fanto method. The glycerol was also estimated directly in the urine by the same method, after the latter had been treated consecutively with silver nitrate, barium hydroxide, and carbon dioxide. Only a faint opalescence was obtained in the silver nitrate in the glycerol estimation in 100 c.c. in both cases—no more than was obtained in blank experiments. The conclusion is drawn that the urine contains no free glycerol.

S. B. S.

The Detection of Peptides in Urine by means of the *p*-Cresol-tyrosinase Reaction. R. CHODAT and R. H. KUMMER (*Biochem. Zeitsch.*, 1914, 65, 392—399).—All normal urines give

a positive reaction with the *p*-cresol-tyrosinase reagent; all urines investigated contain polypeptides, but no tyrosine or peptides yielding tyrosine were found. There is also found in urine a thermolabile substance which inhibits the action both of tyrosinase and trypsin. S. B. S.

Studies on Water Drinking. XVIII. Relation Between Water Ingestion and the Ammonia, Phosphate, Chloride, and Acid Excretion. D. W. WILSON and P. B. HAWK (*J. Amer. Chem. Soc.*, 1914, 36, 1774—1779).—Earlier experiments (Wills and Hawk, this vol., i, 223) showed that an increased ingestion of water resulted in a proportional increase in the ammonia excreted in the urine. A further study of this question has now been made, and also of the relationship of the ammonia output to the chloride, phosphate, and acid excretion.

The amount of ammonia excreted again increased with increased ingestion of water. The excretion of chlorides showed only a small variation with the amount of water taken, and, at certain points in the experiments, a retention of chlorides was observed, which was probably due to the effort of the body to maintain the normal osmotic pressure in its various fluids. A similar retention occurred in the case of the phosphates and acids, but, in spite of this tendency to obscurity, the small differences observed were sufficient to show significant increases in the output of both phosphates and acids after the ingestion of large quantities of water. E. G.

Studies on Water Drinking. XIX. Intestinal Putrefaction as Influenced by the Ingestion of Softened and Distilled Water. C. P. SHERWIN and P. B. HAWK (*J. Amer. Chem. Soc.*, 1914, 36, 1779—1784).—Experiments are described which show that both softened and distilled water, when taken with meals in quantities of 500—1000 c.c., tend to cause a decrease in putrefactive processes in the intestine as indicated by the urinary indican excretion. It is noteworthy that when the greatest decrease in the indican output occurred, that is, during the period of copious drinking, the ethereal sulphates excreted showed a marked increase. This failure of the indican and total ethereal sulphate values to run parallel to one another affords evidence in favour of the view that indican has a different origin from the other ethereal sulphates. E. G.

The Chemical Composition and Physical Properties of the Urines of Ducks and Fowls. KORNELIUS SZALÁGYI and ALEXANDER KAWRUSCHA (*Biochem. Zeitsch.*, 1914, 66, 122—138).—The urine was in both cases obtained from pre-anal fistulae. The following factors were determined: total nitrogen, ammonia, carbamide, uric acid, proteins, amino-acids (by van Slyke's method), colloidal substances (by Salkowski's method), carbon (by wet method), caloric values, composition of ash, acidity, specific gravity, osmotic pressure (by freezing-point method), electrical conductivity, surface tension, viscosity, refraction, and rotation of polarised light. S. B. S.

The Colloidal Nitrogen of the Urine and its Significance for the Clinical Diagnosis of Carcinoma. P. L. J. DE BLOEME, S. P. SWART, and A. J. L. TERWEN (*Biochem. Zeitsch.*, 1914, 65, 345—359).—The nitrogen precipitable by Kojo's zinc sulphate method was estimated, and also the purine substances and uric acid contained in this precipitate. In cases of carcinoma, no very definite differences could be detected in the analyses which would serve any purpose of clinical diagnosis. It was found, however, that the amount of non-dialysable nitrogenous substances in the zinc precipitate was considerably higher than that found in the normal.

S. B. S.

Bactericidal and Antitoxic Action of Lanthanum and Thorium Salts on the Cholera Vibrio. Therapeutic Action of these Salts in Experimental Cholera. ALBERT FROUIN and D. ROUDSKY (*Compt. rend.*, 1914, 159, 410—413).—After mixing the microbic emulsion with an equal volume of lanthanum sulphate or thorium sulphate solution, centrifuging the mixture after thirty minutes, and suspending the microbic deposit in a volume of saline solution equal to that of the original emulsion, a guinea-pig was able to survive a peritoneal injection of an amount equal to twice that which proved fatal in eight hours without previous treatment. An injection of three and a-half times the fatal dose killed the guinea-pigs at the end of twenty-four to thirty-six hours when using lanthanum sulphate, but they survived this amount after its treatment with thorium sulphate. Phagocytosis and dissolution of the vibrio in the peritoneum of the guinea-pig is much more rapid in the case of the cultures treated with the above salts. In the case of monkeys, the culture was administered by the mouth after the purgative effect due to an ingestion of sodium sulphate had been produced, and then either six or twelve hours later 40 c.c. of a 2% solution of thorium or lanthanum sulphate was given by the mouth. In the case of the six hours' intervals, the monkeys survived after treatment with either of the salts, but with the twelve hours, the animals died when lanthanum sulphate was administered, but survived when thorium sulphate was used.

W. G.

The Combustion of Sugar in Pancreatic Diabetes. III. The Sugar Consumption in the Surviving Intestine taken from Dogs with Pancreatic Diabetes. F. VERZÁR and J. KRAUSS (*Biochem. Zeitsch.*, 1914, 66, 48—55).—The consumption of sugar by the surviving intestine of dogs suspended in oxygenated Tyrode's fluid to which dextrose had been added was investigated. Intestines from both normal and depancreatized animals were employed. The results obtained were somewhat irregular, little consumption of sugar occurring, as a rule, in the first two hours. No differences could be detected, however, between the sugar consumption of the organs of the normal and depancreatized animals. Sugar did not stimulate the movements of the intestines as it does that of rabbits.

S. B. S.

The Combustion of Sugar in Pancreatic Diabetes. IV. The Disappearance of the Blood-sugar after Evisceration of Normal Animals and Animals with Pancreatic Diabetes. J. KRAUSS and M. SEINER (*Biochem. Zeitsch.*, 1914, 66, 56—62).—There is a disappearance of the blood-sugar after evisceration both of normal and depancreatized animals. The authors confirm in this respect the results of Macleod and Pearce. They direct attention to the fact, however, that it is not justifiable to draw from these experiments the conclusion that sugar can be destroyed in the blood of depancreatized animals.

S. B. S.

The Combustion of Sugar in Pancreatic Diabetes. V. F. VERZAR (*Biochem. Zeitsch.*, 1914, 66, 75—94).—It has been shown that injection of dextrose increases the respiratory quotient of normal animals, but not of depancreatized animals. The possible explanation of this fact is that the depancreatized animals have lost their capacity for burning sugar. There is, however, another possible explanation, viz., that the organism is already overlaid with sugar, and therefore the injection of further quantities cannot increase the respiratory quotient. The experiments seem to indicate that the latter explanation is not correct, for if sugar is injected into animals shortly after the removal of the pancreas (one or two days), injection of sugar still causes a rise in the respiratory quotient, although there is marked hyperglycæmia. The power of burning the increased sugar injected is only lost some days after the removal of the pancreas. Similar results were obtained with levulose.

It has been shown by Macleod and Pearce that when the liver is excluded from the circulation of a depancreatized animal the blood-sugar diminishes. The explanation suggested is that the liver exerts an inhibitory action on the sugar destruction, but that this action is paralysed by the pancreas. If this explanation is correct, then the injection of dextrose into a depancreatized animal in which the liver is excluded from circulation should give rise to a higher respiratory quotient. The experiments of the author, however, show that this does not take place. After reviewing various experiments on the subject, he draws the conclusion that an animal with pancreatic diabetes can in some way cause the sugar to disappear, but that it has lost the power of burning it completely so as to yield carbon dioxide.

S. B. S.

Physiological Action of Aromatic Mercury Compounds. IV. FERDINAND BLUMENTHAL and KURT OPPENHEIM (*Biochem. Zeitsch.*, 1914, 65, 460—478).—Details are given of the action of a large number of mercury compounds after single and repeated injections into animals. Compounds in which the mercury is both masked and ionised were used. The organs were examined to determine the presence of the mercury. It was found that the liver was the only organ in which the metal was constantly stored, and this happened in all cases with the exception of colloidal mercury and the sodium and mercury salts of diaminodiphenylcarboxylic acid. It appears as if the diamino-group inhibits the deposition of the

metal in the liver. In toxynone (sodium acetylaminomercuribenzoate) this does not happen, as a hydrogen atom of the amino-group is in this case replaced by acetyl. There is no relationship between the toxicity of a compound and its affinity for the tissues. It is assumed that the mercury acts therapeutically by being taken up in the liver, and there converted into a product toxic to spirochetes. As a result of the work on mercury compounds generally, the conclusion is drawn that there is no organic mercury compound which surpasses in its action for the treatment of syphilis the ordinary inorganic medicaments in the same way that salvarsan and atoxyl surpass ordinary arsenic compounds in the treatment of syphilis and sleeping sickness respectively. If such an organic compound might be chosen for therapeutic purposes it is toxynone, as it can be applied intravenously with advantage. S. B. S.

The Behaviour of Glycuronic Acid in the Organism. JOHANNES BIBERFELD (*Biochem. Zeitsch.*, 1914, 65 479—496).—The glycuronic acid was produced by the hydrolysis of menthyl glycuronate, which was obtained by the administration of menthol to rabbits. When administered to rabbits or dogs parenterally (either subcutaneously or intravenously), the acid is excreted almost quantitatively in the urine after a short interval. The same happens to the glycuronic acid produced after administration of menthol or amylene hydrate. Gluconic and saccharic acids are also rapidly excreted in the urine even after parenteral administration of only small doses. Long-continued administration of menthol is only tolerated on a mixed diet, and not on a diet of oats alone. The production of the conjugated acids stops, in the case of rabbits, after a relatively short interval. S. B. S.

Origin of Creatine in the Animal Body. II. The Behaviour of ϵ -Guanido-, ϵ -Carbamido- and ϵ -Amino- n -hexoic Acids in the Rabbit's Body. KARL THOMAS and M. H. G. GOERNS (*Zeitsch. physiol. Chem.*, 1914, 92, 163—176).—Feeding rabbits with ϵ -guanido-hexoic acid did not lead to an increase of the creatinine in the urine, only small amounts of unaltered acid and of a compound, which was found to be ϵ -carbamido-hexoic acid, being isolated. ϵ -Carbamido-hexoic acid was prepared synthetically from ϵ -amino-hexoic acid and urea by boiling with barium hydroxide in a similar manner to that employed by Lippich (A., 1908, i, 861) for the preparation of the carbamido-compounds of the α -amino-acids. The product was obtained in 88% yield as colourless needles, which, after recrystallisation from water, decomposed at 174—178°. Analysis agreed fairly well with the formula $C_7H_{14}O_3N_2$. Hydrolysis with barium hydroxide was carried out in a sealed tube at 140° for four and a-half hours, ammonia and ϵ -amino-hexoic acid being produced. The carbamido-acid was boiled for two hours with concentrated hydrochloric acid without undergoing any change; it thus differs from the α -carbamido-acids of Lippich, which in similar circumstances form hydantoin derivatives.

ϵ -Carbamidohehoic acid administered to rabbits proved to be slightly toxic. About 50% of the acid was regained from the urine, the remainder being utilised in the body. No intermediate products of its metabolism, such as ϵ -aminohehoic acid, could be detected.

The ingestion of ϵ -aminohehoic acid was also followed by toxic symptoms, and 17% of the amount eaten was recovered from the urine.

The results show that the ϵ -guanidohehoic acid metabolised by the rabbit is not first hydrolysed to ϵ -aminohehoic acid, but probably becomes oxidised to the lower homologue, ϵ -guanido-butyric acid. Since, further, the administration of ϵ -aminohehoic acid does not lead to the elimination of ϵ -carbamidohehoic acid, the production of this latter substance from ϵ -guanidohehoic acid in the organism cannot occur through the intermediate formation of ϵ -aminohehoic acid.

H. W. B.

The Action of β -Iminoazolyethylamine [4- β -Aminoethylglyoxaline] and of p -Hydroxyphenylethylamine on Unstripped Muscle. G. QUAGLIARIELLO (*Zeitsch. Biol.*, 1914, 64, 263—284. Compare Dale and Laidlaw, A., 1911, ii, 137).—The author has investigated the action of these drugs on the unstripped muscle fibres of the large and small intestine, uterus, artery, and bronchus, the results being recorded graphically. 4- β -Aminoethylglyoxaline causes contraction, which may be observed even at a dilution of 1 in 17,500,000 by direct action on the muscle fibres. p -Hydroxyphenylethylamine acts indirectly through the nervous system, and thus resembles adrenaline in its sympathomimetic action. These results confirm the previous work of Dale and Laidlaw (*loc. cit.*).

H. W. B.

The So-called Veratrine Contraction. The Action of Aldehydes on the Contraction of Striped Muscle. FRITZ VERZAR and MAGDA FELTER (*Physiolog. Archiv*, 1914, 158, 421—442).—The authors find that formaldehyde, glyoxal, acetaldehyde, paracetaldehyde, acraldehyde, and glyceraldehyde produce the same effect as veratrine on the contraction of voluntary muscle. Other aldehydes, including propaldehyde and higher aldehydes and benzaldehyde, are inactive. Some electrolytes, organic acids, and alkaloids also resemble veratrine in producing a delayed relaxation of the contracted muscle fibre, whilst other allied substances are inactive. The results lead the author to suggest that the secondary chemical tetanus brought about, according to von Frey, by the stimulating action of the compound formed by veratrine and an unknown product of muscular contraction, is really due to the stimulating action of veratrine itself acting on the muscle in the hypersensitive state induced by, and immediately following, a contraction.

H. W. B.

Chemistry of Vegetable Physiology and Agriculture.

The Metabiotic Action of Ultra-violet Rays. Modification of the Morphological and Biochemical Characteristics of the Anthrax Bacillus. Heredity of Acquired Characteristics. (MME.) VICTOR HENRI (*Compt. rend.*, 1914, 159, 340—343).—After exposure to ultra-violet rays, several changes are noticeable in the morphological character of the anthrax bacillus. The least stable character is the chain formation of rods. After exposure to the rays, fragmentary filaments, and even isolated elements, could be observed. Then the form of the rods is altered. After irradiation, instead of the elongated rods, cocci, or cocci mixed with more or less elongated rods, are obtained. After irradiation the rods are diminished in diameter, three new forms composed of very slender elements about one-third the size of the normal elements being obtained. The biochemical characteristics similarly undergo alteration. The normal form is stained by Gram's reagent, but after irradiation five forms were obtained which would not take this reagent. The normal anthrax bacillus is white, but after irradiation two new forms were obtained, which gave intense yellow cultures. These new characteristics remained fixed even after 130 to 200 days, new cultures being taken almost daily. It should be noted that when, by culture on special sugar media, fragmentary filaments or cocci are obtained without irradiation, these forms do not remain fixed, but return to the original form by sowing on to an ordinary medium. After inoculation into a guinea-pig of these modified forms, cultures have been obtained from its blood which had all the macroscopic characters of the normal bacillus. Under the microscope the filaments were fragmentary, but the bacillus sporulated actively. W. G.

The Metabiotic Action of Ultra-violet Rays. Theory of the Production of New Microbic Forms by the Action on the Different Nutritive Functions. VICTOR HENRI and (MME.) VICTOR HENRI (*Compt. rend.*, 1914, 159, 413—415).—A comparative study of the development of normal anthrax bacillus and two new forms, (1) cocciform- S_1 , taking Gram's reagent; (2) slender filaments, not taking Gram's reagent, yellow in colour, which they call anthrax- γ (compare preceding abstract). The culture media consisted of mineral salts, together with (a) one of the carbohydrates, dextrose, sucrose, maltose, lactose, or starch; (b) one of the nitrogenous substances, ammonium lactate, ammonium citrate, glycine, α -alanine, asparagine, or Chapoteaut's peptone; (c) hydrochloric acid or sodium hydroxide at a concentration of $N/200$.

Normal anthrax does not develop on media containing ammonium salts or amino-acids as the nitrogenous nutrient, but only in media containing peptone. The form S_1 behaves exactly like normal anthrax. Anthrax- γ develops in the presence of both ammonium salts and amino-acids. None of the three forms develops

in an acid medium, but all prefer an alkaline to a neutral medium. Normal anthrax develops better on a medium devoid of carbohydrates than in the same medium with carbohydrates present, and if grown under the latter conditions a whole series of modified forms is obtained. For the form S_1 there is no appreciable difference. Anthrax- γ develops best in the presence of carbohydrates, and often it will not grow in a medium containing peptone unless sucrose or maltose are present. Cultures of anthrax- γ are very abundant on potato.

After short periods of irradiation, cultures inoculated on media devoid of carbohydrate develop but little, whereas the culture is abundant in the presence of carbohydrate. For longer periods of irradiation the reverse is true.

Apparently, under the influence of the irradiation, the anthrax bacillus loses its capacity for secreting proteolytic enzymes whilst retaining the power of producing amylolytic enzymes. Such a bacillus placed on a nutritive medium would require carbohydrates for its development, and would thus change its mode of feeding, and as a result its form and all its biochemical and biological properties would be modified. A new form would thus be obtained which would retain its acquired characteristics through thousands of generations.

W. G.

Nitrogen Fixation by *Azotobacter* in Substrata Poor and Rich in Nitrogen. J. HANZAWA (*Centr. Bakt. Par.*, 1914, ii, 41, 573—576).—Mixed cultures of different strains of *Azotobacter* were found to be more efficient than the same bacteria in pure cultures, especially in aqueous solutions of mannitol.

The nitrogen of humus and small amounts of nitrates were almost without effect on the fixation of nitrogen by pure cultures of *Azotobacter*. In presence of nitrogen amounting to 2.5% of the amount of carbon, nitrogen fixation is retarded, and with large proportions of nitrogen, inhibited. Under natural conditions it seems probable that soil nitrogen can only seldom, if at all, have an unfavourable action on nitrogen fixation.

Some humus substances seem capable of being utilised as source of energy in the fixation of nitrogen. The humus of farmyard manure gave positive results, whilst that of green manure gave negative results.

N. H. J. M.

Nitrogen Metabolism of Soil. H. H. GREEN (*Centr. Bakt. Par.*, 1914, ii, 41, 577—608).—Experiments on ammonification, nitrification, nitrogen fixation, and decomposition of cyanamide, both in soils and in solutions inoculated from soil samples taken at approximately monthly intervals from August, 1912, to August, 1913.

As regards the ammonification of organic manures, bacterial activity showed a rise from August to October, a tendency to fall or remain constant in November, and a rise to a maximum in December. In February activity reached the minimum, and from April to July there was a slight fall, probably continued to a summer minimum in August. The nitrification results were similar, except that the spring maximum was in March, whilst the

decline to a summer minimum commenced in April. The slight variations and the December maximum are attributed to the mild character of the winter of 1912—13. Nitrogen fixation in 1% mannitol was low in August and September; subsequently it was fairly constant, except with samples taken after ploughing. No definite results were obtained in the cyanamide experiments.

Comparison of the results of field-manuring experiments with those of laboratory tests indicates that the latter may be of considerable value in supplying information as to the decomposition processes in soils.

Solution methods were found to be equal to those in which the natural soil is employed as medium, whilst as regards nitrification the solution method gave much clearer indications of seasonal variation.

N. H. J. M.

Antagonism between Anions as Affecting Soil Bacteria.

C. B. LIPMAN and P. S. BURCESS (*Centr. Bakt. Par.*, 1914, ii, 41, 430—444).—A study of the effects of reciprocal doses of sodium chloride, sulphate, and carbonate on nitrification in the soil. One hundred grams of sandy soil were mixed with 1 gram of dried blood, moistened, and incubated at 30° for one month; at the end of this period nitrates were determined by the aluminium reduction method.

From the results it would appear that marked antagonism exists between the anions of the three salts when the nitrifying power of the soil is the criterion. For the active transformation of organic nitrogen certain combinations of these three common alkali salts are permissible in the soil without retardation, but even with stimulation of the processes of ammonification and nitrification. Thus both ammonification and nitrification may proceed normally in the presence of a total salt content of 0.45%, consisting of 0.20% chloride and 0.25% carbonate. If sodium carbonate is present to the extent of about 0.1%, either 0.2% chloride or 0.35% sulphate may be added to it, and still permit of efficient nitrogen transformation. The work gives definite indications for the combination of alkali salts as a measure in alkali land reclamation.

H. B. H.

Chemical Actions of Citromyces: Utilisation of Nitrogen Compounds and Action of Heavy Metals in the Medium.

F. ALEX. McDERMOTT (*Chem. Zentr.*, 1914, i, 1893; from *Mycol. Zentr.*, 3, 159—160).—Experiments on the utilisation of uric and hippuric acids and hexamethylenetetramine as sources of nitrogen for *Citromyces glaber* and *C. Pfefferianus*. Development was more rapid in presence of manganese acetate and uranyl acetate, whilst ferric chloride and zinc chloride had a retarding effect.

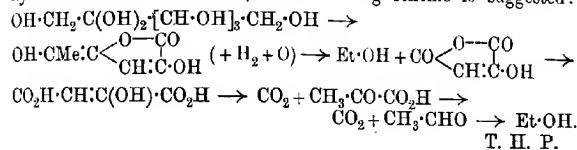
N. H. J. M.

Fermentation of Certain Sugars by means of *Aspergillus glaucus*, and Considerations on Alcoholic Fermentation. F. TRATTA-MOSCA (*Ann. Chim. Applicata*, 1914, 1, 477—492).—Sucrose

is fermented slowly by *Aspergillus glaucus*, and when the solution becomes optically inactive it is found to contain the γ -lactone of a trihydroxyhexadienoic acid.

This lactone, $\text{OH} \cdot \text{CMe} \cdot \text{C} \begin{smallmatrix} \text{O} \\ \diagup \\ \text{CH} \cdot \text{C} \cdot \text{OH} \end{smallmatrix}$ (?), forms white, prismatic needles resembling glass-wool, m. p. 154° , and assumes a violet tint in the light. It is acted on by permanganate, and exhibits normal cryoscopic behaviour in water. In alcoholic solution and in presence of palladium-black it takes up 4H at the ordinary temperature, and it yields a *diacetyl* compound, $\text{C}_8\text{H}_4\text{O}_4\text{Ac}_2$, long, white needles, m. p. 102° , and a *dibenzoyl* compound, $\text{C}_8\text{H}_4\text{O}_4\text{Bz}_2$, white crystals, m. p. 134 – 135° . It combines with bromine, giving a compound, m. p. 99° , and gives a crystalline, sky-blue copper salt, $\text{Cu}(\text{C}_8\text{H}_3\text{O}_4)_2 \cdot \text{H}_2\text{O}$.

The lactone undergoes fermentation by beer-yeast, yielding alcohol and carbon dioxide, and the author considers it probable that it is formed as an intermediate product in ordinary fermentation, its formation being due to simultaneous reduction and oxidation of the sugar molecule. Thus, for the fermentation of the hydrated form of laevulose, the following scheme is suggested:



T. II. P.

Analogy between the Nutritive Value of Different Substances for *Penicillium glaucum* and their Narcotic Action. H. I. WATERMAN (*Chem. Zentr.*, 1914, i, 1844–1845; from *Folia Microbiol.*, 2, Heft 3).—Several narcotics, such as phenol, *m*- and *p*-hydroxybenzoic acids, and protocatechuic acid, in solutions of low concentration, are very suitable as sources of carbon for *Penicillium glaucum*.

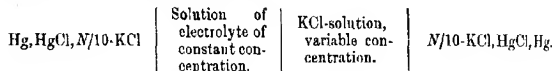
N. H. J. M.

Causes of the Growth of Plants. III. G. A. BOROVIKOV (*Kuloid. Zeitsch.*, 1914, 15, 27–30. Compare A., 1913, i, 324, 571).—Observations have been made on the rate of growth of seedlings in water and in solutions of various electrolytes with the object of ascertaining the connexion between this and the concentration of the cell sap, which was determined by the freezing-point method. The results show that, in general, an increase in the rate of growth is accompanied by a slight reduction in the concentration of the cell sap. This relationship is considered favourable to the view that the swelling of the protoplasmic colloids as a result of the absorption of water is one of the most important factors concerned in the growth of plants. It is supposed that the protoplasm passes through three different stages during the growth of the cell, these stages being distinguished as the solid, the gel, and the sol phases.

The Mechanism of the Exchanges Between the Plant and the Exterior Medium. P. MAZÉ (*Compt. rend.*, 1914, 159, 271—274).

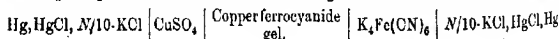
—The author has grown maize plants in aseptic mineral solutions containing 2 or 5% of sucrose. When the concentration of the sugar had reached to such a degree that the plants only tolerated it with difficulty, they lost their turgescence in sunlight and suffered from a lack of water. At this stage the sugar content of the nutritive solution and of the juices of the roots, stem, and leaves was determined. The results showed that there was no relationship between the sugar content of the nutritive solution and of that of the different plant juices. The author draws the conclusion that the laws of osmosis do not entirely control the exchanges taking place, but that it is the chemical work of the plant which controls them. By suppressing this chemical work as far as possible by growing the plants in diffused light, results were then obtained showing a fairly close relationship between the sugar content of the nutritive solution and of the different juices. From this he draws the conclusion that the plant, instead of enriching itself in sugar, lives on its reserves. Further, that the plant constitutes a system permeable to water and to substances that it contains in solution or colloidal suspension, but that the permeability is capable of regulation, not only in the organs which are in contact with the external medium, but also in the different tissues which compose the plant. W. G.

The Theory of the Bioelectric Current. H. ROHONYI (*Biochem. Zeitsch.*, 1914, 66, 248—257).—A series of electrometric measurements were carried out with the chain



As a result, the conclusion is drawn that Loeb and Beutner (A., 1912, ii, 663, 1087; 1913, ii, 801, 802; this vol., i, 357) are in error in holding as characteristic the changes in the so-called bioelectric potential with changes in the salt concentration; these are produced in any chain containing an aqueous salt solution and a salt-free aqueous or non-aqueous solution of an electrolyte. The explanation of the phenomena offered by Loeb and Beutner, which involves the assumption of a plasma membrane of lipid character, is not therefore necessary. It is sufficient to assume that the membrane contains none or only small quantities of salt ions, but has adsorbed in traces electrolytes of acid character. S. B. S.

The Permeability by Ions and the Membrane Potential. H. ROHONYI (*Biochem. Zeitsch.*, 1914, 66, 231—247).—The permeability of membranes by ions does not indicate that there are marked differences in the rate of wandering of the ions through that membrane. It was shown by experiment that the *E.M.F.* of a precipitation membrane investigated in an ordinary chain,



is an ordinary diffusion *E.M.F.* The membrane in the chain plays the same part as an electrolyte-free aqueous medium, and the *E.M.F.* is the same if the membrane is replaced by water in the above chain. The membrane in this experiment was prepared by passing a capillary U-tube from the copper sulphate to the ferrocyanide solutions and allowed to form at the end of the U-tube.

S. B. S.

Influence of Various Salts on Heliotropism. INES MARCOLOGO (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1913, [iii], 19, 226—235).—Examination of the influence of various nitrates, phosphates, and sulphates of potassium, sodium, calcium, and magnesium on green and etiolated seedlings of *Sinapis alba*, *Avena sativa*, and *Phaseolus multiflorus* shows that these salts enhance the heliotropism and shorten the time of reaction of the etiolated plants, but diminish the heliotropism and increase the time of reaction of the green plants. The maximum retardation or prolongation of the time of reaction and the greatest effect on the heliotropism are produced by a solution containing potassium, calcium, and magnesium cations, and the anions of nitric, phosphoric, and sulphuric acids. These influences are to be attributed to chemical actions of the nutritive salts, but there may be also a physico-chemical effect due to the concentration of the liquid, since sodium chloride exerts an action analogous to some extent to that of the above salts.

T. H. P.

Distribution of Compounds with Simple Carbon Chains in the Vegetable Kingdom. HEINRICH FINCKE (*Zeitsch. Nahr. Genussm.*, 1914, 28, 1—9).—Amongst the carbon compounds with unbranched open chains occurring in plants, those with two, six, and eight carbon atoms are the most widely distributed. With regard to the formation of other substances, the compounds with two and six carbon atoms are the most important. This, and the genetic relation of the various carbon chains to one another, is in accordance with the assumption that a 'double carbon chain, glycolaldehyde, is an important intermediate compound in the assimilation of carbon dioxide.

W. P. S.

Importance of the Alkaloids of *Papaver somniferum* for the Life of the Plant. A. MÜLLER (*Arch. Pharm.*, 1914, 252, 280—293).—The function of alkaloids in plants is an unsolved problem. Are they excretory products with a protective function? Are they produced, during the chemical processes occurring in the plant cells, from complex nitrogenous compounds, and then remain as essentially unimportant debris, or can they again be employed in chemical transformations, especially for the regeneration of albumin?

Although the first query might be answered affirmatively for several reasons, as, for example, the fact that alkaloids are usually localised in the peripheral parts of plants, yet the theory is opposed to other equally well-known facts, for example, an alkaloid may be fatal to one creature and innocuous, or nearly so, to another.

The author attempts to answer the second query by an examination of the poppy in the following manner. In the first place, poppy seeds do not contain any alkaloids. The scheme he adopts is to estimate the alkaloidal nitrogen in the whole plant, and also in its various organs at different periods of its growth, in plants grown under natural conditions, and also in others cultivated in a non-nitrogenous nutrient solution. Methods are described for the quantitative extraction of the alkaloids and for the estimation of their nitrogen by Kjeldahl's process. The experiments must be repeated at the same period of growth in different years, because the alkaloidal content is materially affected by weather conditions, the amount decreasing in wet or cloudy weather and increasing in sunny weather.

It is found that in plants grown under natural conditions alkaloids can be detected in the plant about fourteen days after germination; the amount increases (subject to fluctuations caused by weather conditions) until after blooming the swelling of the seeds by reserve albumin begins. As the seeds ripen, the amount of alkaloid decreases in the capsules, stem, and leaves without, however, completely disappearing.

The cultivation of the plants under artificial conditions is effected by cutting through the stem of a blooming plant above the root under water and placing the plant in a non-nitrogenous nutrient solution. As it was found that alkaloids do not pass into the nutrient solution, the plants only require to have fresh sections cut off every five days, renewal of the nutrient solution, and spraying with distilled water; in this manner they thrive well, and by artificial pollination attain to complete ripeness. A diminution in the alkaloidal content can be detected even after ten days in the whole plant, and also in the leaves and stem. After forty-eight days, when the seeds have ripened, the leaves and stem are quite free from alkaloids, while the capsule walls contain traces which can be detected qualitatively, but are too small to be estimated.

It follows from the preceding that the alkaloids of *Papaver somniferum* are utilised in synthesising albumins during the ripening of the seeds, and therefore are not specific excretory products.
C. S.

Constituents of *Andrographis paniculata*. KSHITIBHUSHAN BHADURI (*Amer. J. Pharm.*, 1914, 86, 349—354).—This common bitter plant growing throughout the plains of India contains two bitter principles, which may be obtained by extracting the plant with alcohol and distilling the extract with steam; the residue in the flask consists of an aqueous portion, which on cooling deposits yellow-coloured crystals (bitter *A*), and a solid mass, from which a second bitter principle (bitter *B*) may be extracted by hot water. The substance *A* had m. p. 206°, contained hydroxyl groups, and had the formula $C_{19}H_{28}O_5$. The substance *B* consisted of a white amorphous powder, m. p. 185°, and had the formula $C_{19}H_{28}O_5$ [? $C_{19}H_{22}O_5$]; the name *kalmeghin* is proposed for it. A white

substance having acid properties is liberated when substance *B* is treated with an acid. The plant also contains a small quantity of an essential oil and a resin.

W. P. S.

Distribution of Nitrates in *Phytolacca* (*Pircunia dioica*) during the Winter Rest and During Growth. R. SPALLINO (*Ann. Chim. Applicata*, 1914, 1, 502—505).—The results of tests made by means of "nitron" and of diphenylamine show that *Pircunia dioica* is very rich in nitrates, which are, however, not found in the young leaflets at the beginning of spring, when the temperature is still unfavourable. At a later stage the leaflets, like all other parts of the young shoots, contain nitrates in quantity. Subsequently these salts partly disappear, so that: (1) the nitrates function as a reserve material, and (2) the absence of nitrates from the very young leaflets is probably related to the fact that the synthetic processes are still inactive.

T. H. P.

The Physical-chemical Properties of the Alcohol-soluble Proteins of Wheat and Rye. JULIUS GRÖH and GUSTAV FRIEDL (*Biochem. Zeitsch.*, 1914, 66, 154—164).—The following physical methods were employed. Estimations of viscosity, surface tension, rotatory and refractory powers, and protective action on colloids by (a) Zsigmondy's gold method; (b) the protective action on a platinum sol, as measured by the catalytic action of the latter on hydrogen peroxide, a new method not yet described in detail. The gliadin was obtained in fractions by two methods: (a) by the fractional separation from alcoholic solution; (b) by a method described previously by König and Rintelen. It was found, as a result of physical-chemical examination of the fractions, that gliadin consists of only one protein, although fractions may be contaminated by lecithins. The gliadin from strong and weak glutens is identical. Several proteins are contained in the rye meal, which have not been isolated; a protein identical with gliadin was not obtained. It appears as if the rye does not contain gliadin.

S. B. S.

Arsenic and Manganese in Some Plant Products Used as Animal Foods. F. JADIN and A. ASTRUC (*Compt. rend.*, 1914, 159, 263—270. Compare A., 1913, i, 233, 948).—The authors have extended their estimations of manganese and arsenic in plants to the common fodder plants, finding both metals present in every case. The results are tabulated, giving the amounts present in the fresh and dry weights, and in the case of manganese in the ash of lucerne, saintoin, vetches, clover, potatoes, mangolds, poplar leaves, chestnut, rice, maize, barley, oats, bran, meadow hay.

W. G.

Nicotine in the By-products of the Culture of Tobacco. E. CHUARD and R. MELLET (*Compt. rend.*, 1914, 159, 208—210. Compare A., 1912, ii, 979).—A notable quantity of nicotine is contained in the waste products from tobacco grown according to the Swiss method (*loc. cit.*). Experiments have been performed to

determine the effect on the yield of nicotine in these waste products of (1) allowing the axillary buds to grow instead of removing them as formed; (2) only removing the large leaves and leaving in the earth the trunks bearing newly-formed buds; (3) applying sodium nitrate to these plants thus partly harvested. The results show that: (1) the plants not deprived of their buds give a smaller yield of nicotine and of a poorer quality; (2) the yield of nicotine in plants left in the soil after the harvest, and bearing newly-formed buds, is markedly higher than in those completely harvested; (3) treatment with sodium nitrate does not modify the relative yield of nicotine in the different organs of the plant in a regular manner, but increases the total yield of each plant.

W. G.

Properties of Soil Grains and the Plasticity of Soils. ALBERT ATTERBERG (*Koll. Chem. Beihefte*, 1914, 6, 55—89).—A discussion of the properties of soils in so far as these depend on the size of the grains and on the relative proportions of gravel, sand, silt, and clay. According to the manner in which the properties vary with the size of the grain, the most rational basis for a classification of the grains into groups is afforded by the following ranges of the diameter: 2.0—0.2—0.02—0.002 mm.

The methods employed in the mechanical analysis of soils are referred to, and a new form of sedimentation apparatus is described. The final section of the paper deals with the plasticity of clays and the classification of clays according to their "plasticity numbers."

H. M. D.

Volatilisation of Ammonia from Soils. O. LEMMERMANN and L. FRESSENIUS (*Landw. Jahrb.*, 1913, 45, 127—154).—All soils differ from each other in their power of absorbing ammonia, and the action of calcium carbonate on the volatilisation of ammonia from soils is variable, according to the nature of the soil, sometimes increasing and sometimes diminishing the loss of ammonia.

In some soils the effect of calcium carbonate depends on the amount of ammonium carbonate added; in these soils, calcium carbonate acted favourably only in presence of larger amounts of ammonium carbonate, and increased the loss of ammonia when only small amounts of ammonium carbonate were added.

Absorption of ammonium salts, in the soils examined, depends mainly on the exchange of the bases of the zeolitic substances of the soil. The amount of available potassium seems to influence the action of calcium carbonate.

N. H. J. M.

General and Physical Chemistry.

The Emissivity of Metals and Oxides. I. Nickel Oxide (NiO) in the Range 600° to 1300°. G. K. BURGESS and P. D. FOOTE (*Physikal. Zeitsch.*, 1914, 15, 721—723).—The emissive capacity of nickel oxide for monochromatic red light of wave-length $\lambda = 0.65 \mu$ has been found to decrease with rise of temperature between 700° and 1300°. From data obtained at 938°, 1058°, 1159°, and 1255°, it increases with increasing wave-length between $\lambda = 0.5$ and $\lambda = 0.7 \mu$. The curves showing the relationship between the emissive capacity and the wave-length indicate the existence of a broad absorption band in the ultra-red region.

The total emission of the oxide was also measured by means of a radiation pyrometer. Between 700° and 1200° the total emission increases approximately as a linear function of the temperature, but between 1200° and 1300° the rate of increase is appreciably smaller.

H. M. D.

Optical Properties of Yttrium Platinocyanide. S. BOGUSLAWSKI (*Ann. Physik*, 1914, [iv], 44, 1077—1105).—The interference phenomena exhibited by sections of crystals of yttrium platinocyanide are described and explained. Measurements have also been made of the optical constants.

H. M. D.

The Spectrum of Elementary Silicon. SIR WILLIAM CROOKES (*Proc. Roy. Soc.*, 1914, [A], 90, 512—520).—Measurements have been made of the wave-lengths of lines in the spark spectrum of silicon between $\lambda 2124$ and $\lambda 6371$. In the final observations, silicon electrodes were available which contained as much as 99.56, 99.86, and 99.98% of silicon, the impurities present being titanium, iron, and aluminium. These electrodes were used in correcting the lines given by less pure samples of silicon which were employed in the earlier experiments. It is pointed out that the use of silicon electrodes is rendered difficult by the rapid formation of a coating of oxide, which causes the spark to become much less luminous. This difficulty was overcome by frequently removing the electrodes and grinding the surfaces with an emery wheel.

The wave-length numbers are compared with and discussed in reference to the data obtained by previous observers.

H. M. D.

Ultra-red Spectra. II. A Direct Measurement of the Magnitude of Energy Quanta. NIELS BJERRUM (*Ber. Deutsch. physikal. Ges.*, 1914, 16, 640—642. Compare A., 1912, ii, 1114).—By application of the theory of quanta, it is shown that the frequency of molecular rotation can be obtained from the formula $\nu = n \cdot h / 2\pi^2 J$, in which J is the moment of inertia, n an integer, and h is the fundamental quantum of energy. The rotation frequencies calculated from this formula are in satisfactory agreement.

ment with the values found by von Bahr (A., 1913, ii, 810) in experiments on the ultra-red absorption of hydrogen chloride. From this it follows that the energy of rotation of the hydrogen chloride molecules is represented by $n h \nu$, and that the same unit is involved in the changes of both rotational and vibrational energy.

H. M. D.

Spectrum Analysis by the Secondary Rays from Röntgen Rays and its Application to the Case of Rare Substances. MAURICE DE BROGLIE (*Compt. rend.*, 1914, 159, 304—305).—Using the method already described (compare this vol., ii, 598), the author has determined the number N , as calculated by Moseley's formula, indicating the position of the element in the periodic table, in the case of gallium and germanium, tin and antimony, and lanthanum, using rays belonging to series K . The values obtained correspond well with the positions generally assigned to these elements.

W. G.

The Ultraviolet Spectrum of Aqueous Solutions of Nitric Acid, Metallic Nitrates, and in Particular of Copper Nitrate. G. MASSOL and A. FAUCON (*Compt. rend.*, 1914, 159, 174—175. Compare Hartley, T., 1902, 81, 556; 1903, 83, 221).—Contrary to the results obtained by Hartley (*loc. cit.*), the authors find that copper nitrate falls into line with other metallic nitrates in giving the absorption band of nitric acid, provided that a sufficient thickness of solution is used. The band is, however, less sharply defined, an aqueous solution of copper nitrate being more transparent to the rays between λ 3150 and 2800 than solutions of the other nitrates.

W. G.

The Constant Presence of Rare Earths in the Scheelites, Revealed by Cathodic Phosphorescence. CH. DE ROEDEN (*Compt. rend.*, 1914, 159, 318—320).—The author has examined a number of specimens of scheelite (calcium tungstate) under the conditions given by Urbain and Scal for fluorides (compare A., 1907, ii, 30), and has found bright and dark rays in the spectra of cathodic phosphorescence similar to those attributed by them to the rare earths. All the specimens of scheelite examined contain the rare earths, the relative proportions of these elements varying considerably from one specimen to another. All the rare elements to which this method is applicable were found in one specimen or another, and all the spectral phenomena observed could be explained by the known rare elements.

W. G.

Ultraviolet Spectrum of Neoytterbium. J. BLUMENFELD and G. URBAIN (*Compt. rend.*, 1914, 159, 401—405).—The authors have mapped the arc spectra of the two extreme fractions of the series of eight giving neoytterbium by the method previously described (compare this vol., ii, 731). These two spectra are identical save for a few rays in the one fraction, due to thulium, and a few in the other due to lutecium. There are five hundred rays between

the limits λ 2300 and 3500, and these are given in a list, with their intensity appended to them.

W. G.

The Absorption of Ultraviolet Rays by the Chloro-derivatives of Methane. G. MASSOL and A. FAUCON (*Compt. rend.*, 1914, 159, 314—316. Compare Hartley, T., 1881, 39, 153; Liveing and Dewar, A., 1883, 837; Martens, A., 1902, ii, 117).—The authors have examined three specimens of carbon tetrachloride having respectively b. p. $76.2^\circ/762.4$ mm., $76^\circ/758$ mm., $76.7^\circ/760$ mm. Of these, the first two specimens gave broad absorption bands in the ultraviolet, whilst the third showed no absorption band. Specimen 2 was then submitted to fractional distillation, and a number of fractions were obtained boiling from 61.4° to 76.3° , all of which showed an absorption band. A final fraction was obtained, b. p. $76.4^\circ/758$ mm., which gave no absorption band, and was shown to be pure carbon tetrachloride. The others contained carbon disulphide as an impurity, and this produced the absorption band.

Neither chloroform nor dichloromethane gave absorption bands in the ultra-violet. All three chloro-derivatives are colourless, and transparent to the visible and ultraviolet rays, only absorbing the rays of very short wave-length. The transparency for the latter rays diminishes as the number of chlorine atoms in the molecule increases.

W. G.

The Fluorescence Excited in Gases by Ultra-Schumann Waves. W. STEUBING (*Physikal. Zeitsch.*, 1914, 15, 742—744).—In a previous paper (this vol., ii, 401), Wood and Hemsalech have put forward the view that ultra-Schumann waves are emitted by the spark discharge, and that these give rise to the fluorescence of the gases in the surrounding atmosphere. The author criticises this view, and maintains that no satisfactory proof has yet been given (1) that the fluorescence spectrum is different from that of the exciting spark discharge; (2) that scattering of the light emitted by the spark discharge is eliminated by the experimental arrangement adopted by Wood and Hemsalech; and (3) that ultra-Schumann waves are actually emitted by the spark.

H. M. D.

Theories of Rotational Optical Activity. G. BRUHAT (*Phil. Mag.*, 1914, [vi], 28, 302—304).—A theoretical note in which the theories put forward by Drude and Lorentz on the optical rotatory power are discussed (compare also Livens, A., 1913, ii, 543). It is shown that the two theories hold equally from the point of view of the observable phenomena of anomalous rotatory dispersion and circular dichroism, and their comparison can only be made on the results expected for the dependence of the rotation on the concentration and on the nature of the solvent. Drude's theory points out that the rotatory power is independent of these two factors, whilst Lorentz's theory makes it depend on the mean index of refraction of the active medium according to the relationship $[\omega] = k(\epsilon^2 - 1)[a(\epsilon^2 - 1) + 1]$. This theory does not therefore provide for cases like that of sucrose, in which $[\omega]$ remains constant

at $1/200$, whilst the factor $(\epsilon^2 - 1)(\epsilon^2 + 2)$ varies about $1/3$. The author also cites other reasons why the Drude theory is to be preferred before that of Lorentz.

J. F. S.

Thermodynamics of Photochemical Equilibrium. A. SCHIDLOF (*Arch. Sci. phys. nat.*, 1914, [iv], 38, 31—35. Compare this vol., ii, 601).—A continuation of the theoretical paper previously published (*loc. cit.*). It is shown that a photochemical equilibrium is only dependent on the factor ν/T , in which ν is the frequency of the light and T the temperature of the reaction. A number of corrections in the equations previously published are given.

J. F. S.

The Photochemical Properties of Coloured Resinates. J. LARGUIER DES BANCELS (*Compt. rend.*, 1914, 159, 316—317. Compare A., 1912, ii, 882).—Coloured resinates when exposed to light slowly lose their solubility in benzene. This process is accelerated by the presence of small quantities of mineral salts. Of the chlorides and nitrates of a large number of metals tried, only those of uranium, zinc, and cadmium exert any marked influence, the effect produced being, within certain limits, proportional to the amount of active salt present. The action of uranium is much more powerful than that of zinc or cadmium, which are of the same order. To produce the same effect in the same time, the concentration of zinc or cadmium nitrates requires to be twenty times that of uranium nitrate. The results obtained with uranium and zinc salts are not due to their hydrolysis in aqueous or alcoholic solution giving an acid solution. Certain salts, such as those of copper, iron, chromium, and thorium entirely modify the properties of the resinates, rendering them insoluble, or producing a precipitation which interferes with the experiment.

W. G.

The Magnetic Spectrum of the β -Rays Excited in Metals by Soft X-Rays. H. ROBINSON and W. F. RAWLINSON (*Phil. Mag.*, 1914, [vi], 28, 277—281).—A preliminary account is given of experiments designed to throw light on the connexion between the energy of the β -ray and the frequency of the X-ray exciting it, which may be expected to be connected with it by the relation $E = h\nu$, where E is the energy, ν the frequency, and h is Planck's constant. A nickel anticathode was employed, on account of the relative simplicity of the X-rays from this element. The elements iron and lead have so far been employed as generators of β -rays. The magnetic spectra of the β -rays consisted of bands, not lines; this is ascribed to the production of β -rays at different depths below the surface of the generating metal. The evidence so far obtained points to β -rays being generated which are characteristic both of the element forming the anticathode and of that forming the generator, but it cannot be decided yet whether the simple quantum theory will serve to explain the connexion between the complete β -ray spectrum and that of the X-rays.

F. S.

Spectrum of β -Rays Excited by γ -Rays. SIR ERNEST RUTHERFORD, H. ROBINSON, and W. F. RAWLINSON (*Phil. Mag.*, 1914, [vi], 28, 281—286).—The investigation deals with the velocities of β -rays excited by penetrating γ -rays in various metals, principally lead, and the connexion, if any, between these velocities and those of the primary β -rays accompanying the γ -rays. A fairly thick glass tube containing radium emanation was used as the source of γ -rays, surrounded by a cylinder of the generating metal. A thickness of 0.14 mm. of lead or gold sufficed to obliterate the lines in the magnetic spectrum of the primary β -rays. The bands observed in the spectrum are due under these conditions to β -rays generated in the metal cylinder. They are sharply defined at the edge corresponding with the greater velocity and due to β -rays escaping from the outer surface, and gradually fade in intensity towards the other edge, owing to the loss of velocity of the β -rays which come from the interior.

The most prominent groups of β -rays excited in lead were compared with the strongest groups of primary rays from radium-*B*, having velocities between 0.6 and 0.8 that of light, for which an identity is to be expected on the view that radium-*B* is isotopic with lead. It was found that, within the limits of experimental error, the velocities of the β -rays were the same in each case.

Comparative measurements were made with cylinders of aluminium, silver, gold, and lead around the source. With the first, no groups of β -rays could be detected amidst the general fog; with silver, the lines were faint and difficult to measure; with lead and gold, well-marked lines of similar intensity were obtained. These lines are certainly due to the conversion into β -rays of some of the more penetrating γ -rays of radium-*B*, and their greater intensity with heavy metals is due to the much greater absorption of the γ -rays in these metals than in those of smaller atomic weight. With the silver, comparison with lead revealed no certain difference in the velocity of the three strong groups of rays, but the velocities of a number of the β -rays excited in gold were of the order of 2% higher than those given by lead. F. S.

Excitation of γ -Rays by β -Rays. H. RICHARDSON (*Proc. Roy. Soc.* 1914, [A], 90, 521—531. Compare Chadwick, A., 1912, i, 1025).—The nature of the radiations excited when the β - and γ -rays of radium-*B* and radium-*C* impinge on different substances has been investigated with special reference to the bearing of the results on the type of radiation emitted by different metals on which radium-*C* is deposited. The experiments show that the excitation of characteristic radiations is mainly, if not entirely, due to the β -rays and not to the γ -rays. The amount of γ -radiation excited by the α -rays of radium-*C* is negligible in comparison with that exerted by the β -rays.

From an examination of the radiations emitted by about twenty different elements, it is found that the only radiations excited are those which fall into the *K* and *L* groups found by Barkla. The mass-absorption coefficients for these radiations agree very well with

the numbers obtained previously by Barkla and Chapman (*Proc. Roy. Soc.*, 1912, [A], **86**, 439) for the absorption of the characteristic radiations excited by X-rays.

In addition to the penetrating type of radiation for which the absorption coefficient $\mu=0.115$, radium-C has been found to emit a small amount of soft radiation similar in type to that emitted by radium-B, and for which $\mu=40$ (in aluminium). When radium-C is deposited on different metals, a soft radiation is given out which consists of the characteristic radiation of the metal excited by the β -rays of radium-C, together with the soft radiation emitted by radium-C itself.

H. M. D.

The Spectrum of the Penetrating γ -Radiation from Radium-B and Radium-C. SIR ERNEST RUTHERFORD and E. N. DA C. ANDRADE (*Phil. Mag.*, 1914, [vi], **28**, 263—273).—Previous results for the wave-lengths of the soft γ -rays ($\mu=40(\text{cm.})^{-1}$ Al) from radium-B between the angles of reflection from rock-salt of 8° to 16° showed two lines at 10° and 12° corresponding with the "L" series for lead. By the same method the more penetrating rays, $\mu=0.5$ of radium-B, and $\mu=0.115$ of radium-C, have been examined, and lines found with angles of reflection from rock-salt between $0^\circ 44'$ and $4^\circ 22'$, those greater than $1^\circ 24'$ belonging mainly to radium-B and the others to radium-C. The chief lines are at $1^\circ 0'$ and $1^\circ 40'$, the latter probably a close doublet, $1^\circ 37'$ and $1^\circ 43'$.

A new transmission method was devised to determine these very high-frequency rays with greater accuracy, in which the cone of rays, passing normally through a rock-salt crystal on to a photographic plate beyond, was deprived by reflection of those rays striking the crystal at the reflection angle, leaving blank absorption lines on the corresponding part of the plate, whilst the reflected rays formed dark, reflected lines on another part of the plate. From the position of either the absorption or reflection line and the geometry of the arrangement, the reflection angle could be determined with considerable accuracy. The results are expressed in the following table:

Old reflection method.	New transmission method.		Mean wave-length. ($\times 10^{-9}$ cm.).
	Absorption lines.	Reflection lines.	
$0^\circ 44'$	$0^\circ 42'$	$0^\circ 43'$	0.71
$1^\circ 0'$	$1^\circ 0'$	$1^\circ 0'$	0.99
$1^\circ 11'$	$1^\circ 10'$	$1^\circ 10'$	1.15
$1^\circ 24'$	$1^\circ 24'$	$1^\circ 25'$	1.37
$\{ 1^\circ 37'$	$1^\circ 37'$	$1^\circ 36'$	1.59
$\{ 1^\circ 44'$	$1^\circ 44'$	$1^\circ 44'$	1.69
$2^\circ 0'$	—	$2^\circ 0'$	1.96
—	$2^\circ 20'$	$2^\circ 20'$	2.29
$2^\circ 28'$	—	—	2.42
$2^\circ 40'$	—	—	2.62
$3^\circ 0'$	—	$3^\circ 0'$	2.96
$3^\circ 18'$ *	$3^\circ 18'$ *	—	3.24
$4^\circ 0'$ *	—	—	3.93
$4^\circ 22'$	—	—	4.28

* Possibly second order.

The wave-length of the most penetrating ray, 0.71×10^{-9} cm., is seven times shorter than any previously measured, the "K" line of silver being 0.56×10^{-8} cm., and it is very surprising that the architecture of the crystal is sufficiently definite to resolve such short waves, especially when the thermal agitation of the atoms is remembered. Putting the rock-salt crystal in liquid air did not improve the definition of the lines.

The penetrating γ -rays from radium-B of wave-lengths 1.59 and $1.69 (\times 10^{-9}$ cm.) probably belong to the "K" series for lead, and their wave-lengths agree fairly with that obtained by extrapolation of Moseley's "K" series from aluminium to silver, but the strong line of radium-C, of wave-length 0.99, cannot be the "K" series line for bismuth, the wave-length of which would be only a few per cent. higher than that of lead, and probably belongs to a new series not yet observed, which may be called the "H" series.

A method is given for calculating approximate wave-lengths of γ -rays from the values of the absorption-coefficients, μ , in aluminium. The "hardening" of the γ -rays of radium-C by passage through lead is ascribed to the weeding out of the rays of wave-lengths 0.99 and 1.15, leaving only that of wave-length 0.71.

F. S.

X-Radiation Similar to that from Radium. F. DESSAUER (*Physikal. Zeitsch.*, 1914, 15, 739—741).—In general, the hardness of X-rays is very much less than that of γ -rays, the absorption-coefficients for the former being approximately from ten to eighty times as large as for the latter. An examination of the composition of X-rays has shown, however, that these contain a small proportion of extremely hard rays which resemble closely, and in fact are probably identical with, the γ -rays emitted by radioactive substances. The curve obtained by plotting the intensity of the X-rays as a function of the absorption-coefficient shows that the intensity falls at first very quickly, with diminution in the absorption-coefficient, but at about $\mu = 0.4$ (in aluminium) the rate of decrease in the intensity with diminution of the absorption-coefficient becomes very much smaller. For values of μ less than about 0.35, the curve is but very slightly inclined to the abscissa as compared with its inclination at values of μ from 0.40 to 0.55.

This relationship indicates that X-ray tubes may possibly be utilised as a powerful source of highly penetrating γ -radiation, and may find application for this purpose in medicine.

The factors which exert an influence on the composition of X-rays have been systematically investigated. The proportion of highly penetrating rays is found to increase with decreasing frequency of the discharge, with increase of the potential, and with increasing current density at the cathode. The hardness also appears to increase when the temperature of the cathode rises (within certain limits) and when that of the anti-cathode falls.

H. M. D.

The X-Ray Spectrum of Nickel. W. F. RAWLINSON (*Phil. Mag.*, 1914, [vi], 28, 274—277).—A detailed investigation of the X-ray

spectrum of nickel, which had previously been investigated by Bragg (*Proc. Roy. Soc.*, 1913, [A], 89, 246). The angles of reflection from crystals of rock salt, heavy-spar, and potassium ferrocyanide of the radiations from a nickel anti-cathode were measured. It is shown that the strong α - and β -lines are close doublets, and have angles of reflection as follows: $\alpha=17^{\circ}6'$, $17^{\circ}9'6''$; $\beta=15^{\circ}22'$, $15^{\circ}25'$. These lines were not completely resolved in the first-order spectrum. In addition to the strong α - and β -lines, evidence was obtained of the existence of a series of faint lines between the α - and β -lines. It is shown that in the case of elements belonging to the *K* series of Barkla, a very large proportion of the radiation appears to be concentrated in the α - and β -lines. The absorption of the radiation was measured by means of two electroscopes, and it is shown that with a tube of 30,000 volts 79% of the radiation was absorbed exponentially with a value $\mu/\rho=55.5$ in aluminium. The remaining 21% was absorbed approximately exponentially with a value of $\mu/\rho=10.36$. The radiation became increasingly penetrating as the voltage was raised, and on the assumption that absorption occurred exponentially, it was found that $\mu/\rho=3.25$ at 42,000 volts and 2.54 at 51,000 volts.
J. F. S.

Velocity of Sound in Argon and the Influence of Röntgen Rays. FRANZ STRIEDER (*Ber. Deut. physikal. Ges.*, 1914, 16, 615-616).—The results of measurements of the velocity of sound in argon by Kundt's method indicate that this is not influenced to a measurable extent by the action of Röntgen rays on the gas. This is contrary to the results obtained by Küpper (*Ann. Physik*, 1914, [iv], 43, 905) in experiments with polyatomic gases.
H. M. D.

The Amount of Radium and Radium Emanation Present in the Waters of Several Western Springs. R. W. BOYLE and D. McINTOSH (*Trans. Roy. Soc. Canada*, 1913, 7, iii, 163).—A determination of the radioactivity of the water of the undermentioned Canadian springs by the usual methods has given the following results, expressed in millionths of a milligram of radium per litre: Sinclair, 4.0; Fairmount, 3.5; and Banff, uncertain. In all three cases traces of radium itself were also indicated.
G. F. M.

Thermionic Currents in a High Vacuum. J. E. LILIENFELD (*Physikal. Zeitsch.*, 1914, 15, 744-746).—A reply to a paper with the same title by Langmuir (this vol., ii, 412), in which the author claims priority in respect of certain observations connected with thermionic currents in high vacua.
H. M. D.

Ionisation of Gases by Collision and the Ionising Potential for Positive Ions and Negative Corpuscles. W. I. PAVLOV (*Proc. Roy. Soc.*, 1914, [A], 90, 398-411).—The ionising properties of positive ions have been examined by a direct method. The results indicate that the positive ions emitted by heated sodium phosphate give rise to negative ions by collision with gas mole-

cules. The curves obtained by plotting the ionisation of the gas against the velocity of the positive ions are of the same form for hydrogen, oxygen, and nitrogen, and appear to approach the velocity axis asymptotically.

With a modified form of apparatus, it was found that the ionising potential for positive ions in hydrogen is about 10 volts, which is of the same order of magnitude as the ionising potential for negative corpuscles. Whereas, however, the ionisation velocity curves are straight lines when the ionisation is due to negative corpuscles, the curves are markedly convex to the velocity axis when the ionisation is brought about by positive ions.

The values obtained for the ionising potential of negative corpuscles in hydrogen and helium by Franck and Hertz (A., 1913, ii, 174) have been confirmed by a different method of measurement.
H. M. D.

Action of a Wehnelt Cathode. FRANK HORTON (*Phil. Mag.*, 1914, [vi], 28, 244—252).—Experiments have been carried out to determine whether the emission of electrons from lime in a Wehnelt cathode depends on the nature of the substance on which it is heated, and further experiments have been made to test the separation of calcium and oxygen by the passage of a thermionic discharge from lime, and to determine the connexion between the recombination of these elements and the electron emission. As a result of the experiments, the author comes to the conclusions: (1) That the electron emission from a Wehnelt cathode has its origin in the lime itself, and the lime does not merely serve to help the electrons to escape from the metal. (2) When an electric current passes through lime at a high temperature, the amount of oxygen liberated is only a very small fraction of what would be expected if the conductivity of the lime were entirely electrolytic. It is suggested that the conductivity is entirely electrolytic, and that the products of electrolysis diffuse through the lime and recombine. It appears unlikely, however, that such recombination should occur so rapidly and completely, through a layer of solid lime, especially as the charged oxygen atoms would be liberated on the vacuum side of the oxide layer, and with a strong electric field tending to drag them away from the cathode. (3) The chemical combination of calcium and oxygen does not by itself give rise to any detectable electron emission. From these results it appears improbable that either the theory of Fredenhagen (A., 1913, ii, 903) or that of Gehrts (A., 1913, ii, 1005) can furnish an explanation of the activity of the Wehnelt cathode.
J. F. S.

The Ionisation of Platinum by Cathode-Rays. NORMAN CAMPBELL (*Phil. Mag.*, 1914, [vi], 28, 286—302).—It was found that the ionisation produced by cathode-rays in falling on platinum can be very greatly reduced by prolonged heating of the metal in a vacuum or in oxygen. The heating first produces no effect, then there is a sudden large change, followed by a slow change, of

which the end is never reached. It is probable that ultimately the platinum would not be ionised at all by cathode-rays of less than 40 volts' speed. The metal can be put back into its initial state by bombardment with cathode-rays of 100 volts' speed in a pressure of gas below 0.01 mm., but mere contact of the gas or vapours does not restore it appreciably. This restored condition, however, is much less permanent than initially, and a few minutes heating, instead of a few hours, brings the sudden change.

Thus the same treatment which reduces greatly thermionic and photoelectric effects reduces also the ionisation produced at a metal surface by cathode-rays. An explanation of the effects is offered on the view that hydrogen is present in the metal in two forms, first, condensed on the surface, and, secondly, dissolved in the interior, the sudden diminution of the ionisation by heating corresponding with the abolition of the surface layer and the further gradual diminution to the progressive removal of the dissolved gas. To explain the temporary restoration of the surface by the electric discharge, recourse is had to a surface "double layer." F. S.

The Positive Ionisation from Heated Platinum. CHARLES SHEARD (*Phil. Mag.*, 1914, [vi], 28, 170—187).—The increase of positive thermionic currents from platinum wires in high vacua, produced either by heating the wire, earthed, to a higher temperature than that at which the ionisation is subsequently measured, or by heating it, charged to a negative potential, to a temperature sufficient to cause it to discharge negative electricity, has been re-examined in dry air at atmospheric pressure. Testing the ionisation always at 628°, and heating the wire, earthed, to various temperatures, revealed two maxima, one after previous heating at 654° and the other at 756°. Experiment showed that the negative emission from the wire when heated and charged negatively became appreciable at 760°. The results are interpreted on the theory that, on heating the wire, decomposition of a molecule *AB* occurs with production of two ions, *A* positively and *B* negatively charged, *A* being expelled or stored up, later to be expelled when an electric force is applied. At higher temperature *B* loses its electron. Various effects result in accordance with a number of possibilities, which are too numerous to be considered in an abstract. It is necessary to assume the presence of at least two substances capable of so producing ions on heating.

By heating the wire in the flame of a Bunsen burner, an increased positive emission was also obtained, probably in part due to the removal of a surface material incapable of producing ions and in part due to the hydrogen absorbed, owing to its affinity for electrons. Heating in carbon dioxide decreased, if anything, the positive emission. The decay with time of the positive currents at different temperatures showed the existence of two sources of ions, the first source decaying according to an exponential law and the second increasing to a maximum before decaying. This results in the ionisation-time curves showing a formal resemblance to the decay curves of the radium active deposit. F. S.

Emission of Electricity from Various Substances at High Temperatures. G. W. C. KAYE and W. F. HIGGINS (*Proc. Roy. Soc.*, 1914, [A], 90, 430—437. Compare A., 1912, ii, 525; 1913, ii, 661).

—The emission of electricity by various substances has been investigated at temperatures of 2000—2500° by experiments in a carbon-tube furnace. The effect due to the carbon was eliminated by difference measurements. The substances examined included the oxides of calcium, strontium, barium, magnesium, silicon, aluminium, and iron, and the metals tin, aluminium, iron, copper, and brass. With the exception of brass, all these substances were found to give off large quantities of negative electricity during the volatilisation which occurred at the temperature of the experiments. Without the application of any extraneous potential difference, currents of the order of 4 amperes per cm.² were obtained with barium oxide and alumina. The corresponding value for tin was 2 amperes, and for iron 1, whilst brass gave a current of 0.5 ampere in the opposite direction, indicating the emission of large quantities of positive electricity.

H. M. D.

Absorption of Gases in the Discharge Tube. F. H. NEWMAN (*Proc. Roy. Soc.*, 1914, [A], 90, 499—506).—Experiments have been made on the absorption of gases by the electrodes in discharge tubes, the main object being to ascertain whether there is any connexion between the amount of gas absorbed and the quantity of electricity passing during the discharge.

The liquid alloy of sodium and potassium absorbs nitrogen and hydrogen, whether used as cathode or anode, but the quantity of gas absorbed, relatively to the quantity of electricity passing, is greater when the alloy is made the cathode. Mercury behaves similarly towards oxygen. In all cases the ratio of the absorption to the quantity of electricity passing increases as the pressure of the gas in the discharge tube is reduced.

It is suggested that the gases are transformed into active modifications under the influence of the electric discharge. The active forms then enter into combination with the electrode substances. This hypothesis is supported by the fact that the known active modification of nitrogen is absorbed when passed over sodium-potassium alloy. The greater absorption which is observed when the metals are used as the cathode is probably due to the combination of the positive rays with the metal.

Experiments in which molten cadmium, zinc, bismuth, and lead were tested for absorption of nitrogen gave negative results with the ordinary discharge.

H. M. D.

Conductivity. II. Conductivity of Some Formates and of Hydrogen Chloride in (Anhydrous) Formic Acid. Cases of Apparent Agreement of Strong Electrolytes with the Mass Law. H. I. SCHLESINGER and A. W. MARTIN (*J. Amer. Chem. Soc.*, 1914, 36, 1589—1620).—Schlesinger and Calvert (A., 1912, ii, 26) have shown that solutions of ammonia in anhydrous formic acid are excellent conductors, and that ammonium formate,

although highly ionised, obeys the law of mass action. A study has now been made of the behaviour of sodium, potassium, and phenylammonium formates in anhydrous formic acid. Determinations of the conductivities and freezing points of hydrogen chloride in the same solvent have also been carried out.

The formates in anhydrous formic acid obey the law of mass action up to concentrations of 0.3–0.6 molar if the degree of ionisation is calculated from the conductivity values which have not been corrected for viscosity. The ionisation constants are as follows: sodium formate, 0.816; aniline formate, 0.814; potassium formate, 1.02; and ammonium formate, 1.23. The same is true of solutions of hydrogen chloride, the ionisation constant of which is only 0.04. At higher concentrations than 0.3–0.6 molar the formates show deviation from the mass law, the degree of ionisation being less than it should be. The results also indicate that the greater the value of the ionisation constant, the higher is the concentration at which the deviation begins; thus, ammonium formate begins to deviate above 0.55 molar, potassium formate at above 0.45 molar, and sodium and aniline formates at about 0.3 molar. This suggests that a relationship exists between the degree of ionisation and the volume of the non-ionised molecule.

When the conductivities are corrected for the viscosity of the solutions and the ionisation constants calculated from these corrected values, the agreement with the mass law disappears. Evidence is adduced to show that the uncorrected conductivities of these solutions should be used for the calculation of the degree of ionisation.

The results obtained by Zanninovich-Tassarini (A., 1896, ii, 352) on the conductivities and freezing-point depressions of solutions of hydrogen chloride in formic acid have been found to be incorrect.

E. G.

The Acid Dissociation Constants of the Carbohydrates. L. MICHAELIS (*Biochem. Zeitsch.*, 1914, 65, 360–362).—In the former series of measurements of the acid dissociation constants (Michaelis and Rona, A., 1913, ii, 379) it was found that maltose had a higher value than might have been expected. It is now shown that the preparation used was not pure. A preparation was obtained, therefore, by the slow precipitation of a saturated solution of the sugar in 70% alcohol by ether vapour. For this, the value of k found was 9.0×10^{-13} . This is only slightly greater than that found for the reducing mono- and di-saccharides.

S. B. S.

Potential of Silver in Non-aqueous Solutions of Silver Nitrate. VERNETTE L. GIBBONS and F. H. GETMAN (*J. Amer. Chem. Soc.*, 1914, 36, 1630–1655).—A résumé is given of previous work on the potentials of metals in aqueous and non-aqueous solutions of their salts, and an account is furnished of an investigation of the behaviour of silver in non-aqueous solutions of silver nitrate.

The conductivities of solutions of silver nitrate in ethyl alcohol, methyl alcohol, acetone, aniline, and pyridine have been deter-

ined for concentrations between 0.1*N* and 0.0001*N*. It has been found that the conductivity curve for solutions in aniline approaches a second maximum as the solutions become more dilute. The results also indicate a relationship between the dielectric constant and the normalities of all the conductivity curves. Measurements have been made of the transport numbers of silver nitrate in ethyl alcohol, methyl alcohol, and pyridine. The *E.M.F.* has been determined for a large number of concentration cells in the different solvents, and for these experiments a special form of apparatus was employed, which was free from defects due to capillarity and constant communication of the two liquids. Calculations of the electrode potential of silver gave the following values: in ethyl alcohol, 0.8314; in methyl alcohol, 0.8298; in acetone, 0.9022; and in pyridine, 0.3711. The data obtained in these experiments indicate that the abnormalities observed in non-aqueous solutions of silver nitrate are due to the combination of the solvent and solute to form complex compounds which undergo gradual dissociation. E. G.

Volta Effect and Unimolecular Layers. J. GUYOT (*Compt. rend.*, 1914, 159, 307—311).—The apparent potential difference at the contact of a metal and pure water diminishes notably, and may become inverted by depositing on the surface of the water very thin layers of certain insoluble organic compounds. As each drop of the latter is placed on the water the diminution effect increases, until the surface of the water is entirely covered. At this stage the surface tension is equal to that of pure water, but, on the addition of more drops, the surface tension falls rapidly, whilst the diminution in the Volta effect becomes less and less, and finally disappears. The author has measured this Volta effect in the case of a number of glycerides and their corresponding acids, esters of dibasic acids, dibasic acids, esters of monobasic acids and their corresponding alcohols, metallic salts, an aldehyde, a benzene hydrocarbon, and some aromatic hydroxy- and alkyloxy-compounds. The results obtained are practically the same, whether the pure substance is used or its solution in benzene or toluene. W. G.

Variation of Electrical Potential Across a Semi-permeable Membrane. F. G. DONNAN and G. M. GREEN (*Proc. Roy. Soc.*, 1914, [A], 90, 450—455).—In a previous paper (*A.*, 1911, ii, 848) it was shown that the potential difference between two differently concentrated solutions of an electrolyte, separated by a membrane which is impermeable to the electrolyte, but permeable to the solvent, can be represented by the formula $\pi = RT/nF \cdot \log c_1/c_2$, in which c_1 and c_2 are the molar concentrations of the K^+ ions of the electrolyte *K.A.* In the derivation of this formula, it was assumed that the membrane is permeable to other salts with the same cation K^+ , although impermeable to the salt *K.A.*

Measurements have now been made of the potential difference between two differently concentrated solutions of potassium ferrocyanide, separated by a membrane of colloidal copper ferrocyanide.

In these experiments, $1N$ -solution was combined with solutions varying from $0.1N$ to $0.01N$, and in a second series a $0.1N$ -solution was combined with solutions varying from $0.05N$ to $0.005N$.

On comparing the observed potential differences with those calculated from the above formula, it is found that there is a fairly constant deviation of the order of 25% in all the measurements which involve the $1N$ -solution. A much closer agreement is exhibited by the results for pairs of solutions in which the $0.1N$ -solution is the stronger, although the percentage deviation increases as the ratio of the concentrations increases. When the assumptions involved in the calculation of the potential difference are taken into account, it would seem that the experimental data afford evidence of the correctness of the above formula in its application to the case investigated.

H. M. D.

Thermodynamics of Normal Cells. ERNST COHEN and W. D. HELDENMAN (*Chem. Weekblad*, 1914, 11, 740—746).—A comparison of the results given by von Steinwehr in his paper on the Weston cell (this vol., ii, 622) with those previously obtained by Cohen (A., 1900, ii, 703).

A. J. W.

Electrolytic Deposition of Metals in Valve Cells. GÜNTHER SCHULZE (*Ann. Physik*, 1914, [iv], 44, 1106—1120).—The action of an alternating current on the deposition of copper from a copper sulphate solution, in which a tantalum electrode is immersed, has been examined with special reference to the valve effect. When the tantalum forms the cathode, about 35% of the total copper is deposited in such a condition that it is redissolved in the succeeding phase of the current discharge when the tantalum forms the anode. The remainder separates as a fine powder, and settles at the bottom of the containing vessel. In the initial period of this phase, the soluble copper is redissolved, and the cell then ceases to transmit the current in this direction.

The proportion of soluble copper which is deposited during the passage of the current through the solution to the tantalum is practically independent of the applied potential difference, the current density (at higher densities), the concentration of the electrolyte, and the thickness of the active tantalum layer. It increases with the temperature and with diminution in the current density (at low densities), and also increases as the strength of the acid in combination with the copper decreases.

The proportion of soluble copper is influenced to a large extent by the addition of other electrolytes to the solution, this influence being determined by the valve potential of the added electrolyte. The lower this valve potential, the greater is the diminution in the quantity of deposited copper.

From experiments with solutions of the nitrates, sulphates, and acetates of the heavy metals, it has been found that the proportion of the heavy metal, which is deposited in a soluble form by the same alternating current, varies with the nature of the acid radicle, but in all three cases the numbers obtained afford a series in which the metals are arranged in the same order.

Similar phenomena are exhibited with an aluminium electrode, but the valve-action effects are not so clearly developed in this case.

H. M. D.

Concentration Cells Built up from Ammoniacal Solutions of Silver Salts. A. REYCHLER (*Bull. Soc. chim. Belg.*, 1914, 28, 222—227).—It is shown that the *E.M.F.* of concentration cells of the type $\text{Ag} | \text{ammoniacal silver chloride (1)} | \text{ammoniacal silver chloride (2)} | \text{Ag}$, in which the two solutions have the same ammonia and different silver chloride concentrations, can be calculated from the formula $96540E = 2v/u + v \cdot RT \cdot \log C/c$, in which C is the silver chloride concentration in the stronger, c that in the more dilute, solution.

The *E.M.F.* of cells in which the two solutions have the same silver chloride concentration and contain different quantities of ammonia is similarly given by $96540E = nRT \cdot \log A/a$, in which A and a are the free ammonia concentrations of the concentrated and dilute solutions respectively, and n is the ratio of ammonia to silver in the complex silver salt in the solutions. The calculated *E.M.F.*'s are in satisfactory agreement with the experimental data recorded in the literature if it is assumed that $n = 2$. H. M. D.

Indices of Migration of the Ions and the Transport of Ammonia in Ammoniacal Solutions of Silver Nitrate. A. REYCHLER (*Bull. Soc. chim. Belg.*, 1914, 28, 215—222).—Measurements of the relative mobilities of the positive and negative ions show that the proportion of the current carried by the negative ion increases somewhat when ammonia is added to an aqueous solution of silver nitrate. From experiments with solutions obtained by the addition of ammonia to silver nitrate in the molar ratios 2:1 and 1:1, it has been found that the change in the ammonia concentration at the electrodes indicates respectively the transport of somewhat less than 2 and 1 mols. of ammonia for each silver ion. It is suggested that the complex ions involved in the transport of the electric charge are those represented by the formulae $\text{Ag}'_2\text{NH}_3$ and $\text{Ag}'\text{NH}_3\cdot\text{H}_2\text{O}$, and that the corresponding ion in pure aqueous solution is $\text{Ag}'_2\text{H}_2\text{O}$.

H. M. D.

Indices of Migration of the Ions and the Transport of Ammonia in Ammoniacal Solutions of Copper Sulphate. A. REYCHLER (*Bull. Soc. chim. Belg.*, 1914, 28, 227—229).—The relative mobilities of the ions in aqueous solutions of copper sulphate are practically unaltered on the addition of ammonia. The change in the ammonia concentration resulting from the passage of the current indicates that at least four, and possibly five, molecules of ammonia are associated with the copper ion in the ammoniacal solutions.

H. M. D.

Preparation of Alloys for Magnetic Researches. J. DE FREUDENREICH (*Arch. Sci. phys. nat.*, 1914, [iv], 38, 36—45).—Alloys of iron with nickel and cobalt, corresponding approximately with

the formulae Fe_2Ni and Fe_2Co , have been prepared by melting the two metals together in a magnesite crucible in an electric resistance furnace. Attempts to prepare these alloys by the thermite process from iron oxide and the second metal gave products which contained about 2% of aluminium and 2% of silicon. Such alloys had a magnetic saturation which was considerably smaller than the correct value for the pure alloys, and since no relationships could be deduced between the magnetic saturation and the impurities, the alloys were valueless for the purpose of the author. The magnetic saturation of the ferrocobalt alloy is 10% larger than that of pure iron, whereas the alloys prepared by the thermite process were only 6.5% larger. J. F. S.

Magnetic Susceptibility and Electrolytic Dissociation. A. QUARTAROLI (*Gazzetta*, 1914, 44, ii, 43—63).—The method previously described (this vol., ii, 619) has been applied to the study of the magnetic susceptibility of a number of solutions of iron, manganese, nickel, and cobalt salts, either alone or in the presence of mannitol or ammonium chloride, citrate, or tartrate.

The results show that, although an undeniable relation exists between electrolytic dissociation and magnetic susceptibility, the latter does not depend merely on the free ions of the magnetic elements. Where complex ions are present, the susceptibility may be even greater than with the simple salts. Additional support is thus afforded by the general rule that the contribution of atoms to the physical constants of compounds is a variable dependent on the other atoms present, and probably also on the order of arrangement. T. H. P.

Photographic Analysis of Explosions in the Magnetic Field. HAROLD B. DIXON, C. CAMPBELL, and W. E. SLATER (*Proc. Roy. Soc.*, 1914, [A], 90, 506—511).—The explosion-waves in a series of gas mixtures have been photographed as the waves entered, traversed, and emerged from a magnetic field, and also when they travelled through the same tube in the absence of the magnetic field. The mixtures examined were: (1) cyanogen and oxygen with varying proportions of nitrogen; (2) hydrogen and oxygen in different proportions; (3) acetylene and oxygen; (4) carbon disulphide and oxygen; (5) carbon monoxide and oxygen. In no case do the photographs show any influence of the field on the explosion-wave phenomenon, and since the mechanism of a compression-wave affords a satisfactory explanation of the observed effects, the authors draw the conclusion that the velocity of the explosion-wave is not connected with the ionising action of electrons. H. M. D.

The Dilatation of Ferro-nickels over a Wide Temperature Interval. P. CHEVENARD (*Compt. rend.*, 1914, 159, 175—178).—A study of the dilatation and contraction of alloys of iron and nickel, varying from pure iron to pure nickel, over a temperature

range from -195° to 750° . The difference between the linear dimensions of bars of the alloys before and after heating are a measure of the amplitude of the irreversible transformation. These differences gradually tend towards zero on passing from iron to the alloy Fe_2Ni , which is apparently the limit of irreversible alloys. The alloys between Fe_2Ni and FeNi_2 have abnormal, quasi-reversible properties. For the alloy FeNi_2 , the dilatation takes place according to a parabolic law between 0° and 800° .

W. G.

Determination of the Specific Heat of Chlorine. HERMANN SCHMIDT (*Physikal. Zeitsch.*, 1914, 15, 720).—The author refers to his previous measurements of the velocity of sound in gases, in which the position of the stationary waves in a Kundt tube was made evident by the ionisation of the gas.

H. M. D.

Molecular Complexity at the Melting Point. D. E. TSAKALOTOS (*J. Chim. phys.*, 1914, 12, 461—463).—A theoretical paper in which it is shown that the fatty acids mixed with water constitute binary systems which do not follow the general law put forward by Thole, Mussell and Dunstan (T., 1913, 103, 1108) that binary systems which have positive viscosity curves have also fusion curves which exhibit one or more maxima. The viscosity curves of the lower fatty acids and water are entirely positive, but the fusion curves show no maxima. The author explains the anomaly by the assumption that the molecular compounds formed between the acid and water exist only in the liquid state, and are dissociated as the mixture approaches its freezing point. An associated liquid is also considered as a binary system the constituents of which are alike, and that in certain cases the complex molecules dissociate as the freezing point is reached, in the same way as in the above-mentioned cases.

J. F. S.

Unimolecular Layers and Superfusion. HENRI LABROUSTE (*Compt. rend.*, 1914, 159, 306—307).—In the case of substances such as trilaurein and tribenzoin, which exhibit marked superfusion, the matter obtained by joining together unimolecular layers appears in the liquid state if the substance can exist superfused at the experimental temperature. Fused or superfused substances can be spread out on water having a temperature considerably lower than the melting point of these substances provided that the temperature of the water is higher than the lowest temperature at which it is possible to obtain the substance in the superfused state. These rules do not apply to those substances, such as camphor, which spread out spontaneously on water, even in the solid state, owing to their volatile or soluble nature.

W. G.

An Exact Vapour Pressure Formula. IVAR W. CEDERBERG (*Physikal. Zeitsch.*, 1914, 15, 697—705).—According to van der Waals, the relation between the vapour pressure p of a liquid and

the temperature T may be approximately represented by the formula $\log \pi_0/p = a(\theta_0/T - 1)$, in which π_0 is the critical pressure, θ_0 the critical temperature, and a a constant. It has already been pointed out that a is not constant, but is a function of the temperature. For a number of substances, the curves which are obtained by plotting a as a function of T are found to be convex to the temperature axis, and approximately symmetrical with reference to a line drawn through the 'minimum point on the curve at right angles to the temperature axis. Where this is not the case, the curve may be made symmetrical by an alteration of the critical pressure to an extent which falls within the limits of experimental error. On the assumption that this curve is symmetrical in all cases, it is suggested that the dependence of a on the temperature is represented by $a = a \cdot \beta^{(T/\theta_0 - v)^2}$, in which a is the minimum value of a , β is a constant, and v is the reduced temperature corresponding with the minimum value of a . The resulting formula, $\log \pi_0/p = a \cdot \beta^{(T/\theta_0 - v)^2} \cdot (\theta_0/T - 1)$, is found to afford an exact representation of the vapour pressures of water and benzene from the lowest temperatures up to the respective critical temperatures.

Since the van der Waals' equation may be regarded as a special form of the reduced vapour-pressure equation $p/\pi_0 = F(T/\theta_0)$, it was to be expected that the constants in the above equation would, at least in part, be found to have the same value for different substances. In point of fact, the value of β is approximately equal to 2 and v to $\frac{2}{3}$ for non-associated substances, and for this group of liquids the vapour-pressure formula may be simplified by the introduction of these values. The constant a varies, however, from one substance to another. It is shown that a is connected with the latent heat of vaporisation by means of the formula $a = \frac{2}{3} M \lambda / p(V - v)$, in which M is the modulus of Briggs' logarithms, λ the molecular heat of vaporisation, V the molecular volume of the saturated vapour, and v that of the liquid at the temperature ($v = \frac{2}{3}$) corresponding with the minimum value of a .

H. M. D.

An Apparatus for Boiling-point Determination without Thermometer Correction. THEODOR PAUL and KARL SCHANTZ (*Ber.*, 1914, 47, 2285—2288).—An apparatus is described embodying the principles of Beckmann's boiling-point apparatus and Kahlbaum's still-head; the condenser can, by rotating, be moved from a reflux position to one for direct distillation. Without disconnecting the apparatus in any way, it is therefore possible to determine the boiling point of a mixture first at constant composition and then during distillation. For details the original paper should be consulted.

D. F. T.

Advantageous Form of Still for the Exact Measurement of Boiling Point during Fractional Distillation. THEODORE W. RICHARDS and FREDERICK BARRY (*J. Amer. Chem. Soc.*, 1914, 36, 1787—1791).—Apparatus is described which has been devised for

the exact determination of boiling points. Its essential feature is that the whole stem of the thermometer is maintained at the temperature of the vapour, and the boiling point of the actual distillate can thus be accurately ascertained.

It consists of a flask and a wide tube held parallel to the neck, and connected with the latter by two side-tubes at the top and bottom. The upper side-tube, which forms the exit tube for the vapour, is joined to the upper end of the neck of the flask. The lower side-tube, which serves to return the prematurely condensed liquid to the flask, is a constricted continuation of the end of the wide tube; it is bent into the form of a shallow U, and fused into the neck of the flask at a point a few cm. above the bulb. The wide tube is open at the top, where it is so constricted as to receive and hold closely a Beckmann thermometer at a point near the zero mark. The thermometer can be made to fit without grinding, as a liquid seal will collect at this point and prevent the escape of vapour, but for use with hygroscopic liquids a ground joint must be employed. The wide tube and upper connecting tube are encased in a thick shell of asbestos.

In a second form of the apparatus, suitable for use with small Anschütz thermometers, the upper end of the wide tube is fitted with a glass stopper provided with a hook, from which the thermometer can be suspended.

The apparatus is of simple construction, efficient, and convenient in use, and can be easily cleaned. E. G.

Theory of the Fractional Distillation of Mixtures of Water and Alcohol. E. CHENARD (*Bull. Soc. chim.*, 1914, [iv], 15, 646—649).—A study of the conditions governing fractionation by condensation, which requires, as essential, the continuous removal of the condensed liquid from contact with the vapours producing it. The apparatus consisted of an unpolished copper tube 35 cm. long and 1 cm. internal diameter, bent slightly downwards and fitted midway with a tube for collecting the condensed liquid and exhausting the apparatus. A thermometer at each end of the tube gave the temperatures between which condensation occurred. The ratio of condensed liquid (p) to the total weight of vapour (P) passing through the tube varied with the velocity of flow of the vapour through the tube. This ratio, p/P , was higher with a low velocity, as was also the ratio of condensed alcohol to total alcohol. W. G.

Laboratory Fractionating Apparatus. HENRI VIGREUX (*Bull. Soc. chim.*, 1914, [iv], 15, 682—685. Compare Hildt, this vol., ii, 103).—A comparison of the effectiveness of the Chenard and Vigreux fractionating columns for separating such mixtures as water and alcohol or benzene and toluene by fractional distillation. Length for length, the Vigreux column is far more efficient than the Chenard. W. G.

Heat of Formation of Solid Solutions. H. W. FOOTE and BLAIR SAXTON (*J. Amer. Chem. Soc.*, 1914, 36, 1704—1708).—An account is given of determinations of the heats of solid solution of sodium chlorate in silver chlorate, and of silver chlorate in sodium chlorate. The method employed consisted in determining the heats of solution in water of the mixed crystals and of mechanical mixtures of the same empirical composition. The difference between these two values gives the heat of formation of the mixed crystals from the single salts. Four samples of mixed crystals were prepared by means of Foote's data (*A.*, 1892, ii, 453). Two of the samples were on the sodium chlorate side, and crystallised as cubes, whilst the other two contained an excess of silver chlorate and were tetragonal.

The results show that both the molecular heats of formation of the solid solutions are small and of opposite sign. The values for the isometric crystals are almost constant, showing that there is little or no heat of dilution, but those for the tetragonal crystals show a small variation, indicating that in this case there is a small heat of dilution. The amount of silver chlorate which can be taken up by sodium chlorate to form mixed crystals increases with the temperature, and the process is accompanied by absorption of heat, whereas in the case of the tetragonal crystals the reverse is true. In the relation of the heat of solution to the temperature-coefficient of solubility, Le Chatelier's law is therefore applicable to solid solutions as well as to solutions of other types. E. G.

A Regularity between Molecular Heat of Combustion and its Bearing on the Constitution of the Hydrocarbons. GERVAISE LE BAS (*Chem. News*, 1914, 110, 26—27, 37—38).—The molecular heat of combustion of gaseous, liquid, and solid paraffins is proportional to the number of valency units in the hydrocarbon molecule. From the data for the gaseous paraffins this ratio is equal to 26.5, which is regarded as the effective combustion value of the hydrogen atom. The effective combustion value for combined carbon is therefore $4 \times 26.5 = 106.0$. In the case of the olefines and acetylenes, the observed heats of combustion are greater than those calculated from the effective heat values of carbon and hydrogen, the differences corresponding with the double and triple bonds being +15.8 and +44.3 cal. respectively.

The heats of combustion of cyclopropane and cyclobutane are also greater than the calculated values to the extent of 15.3 and 18.0 cals., whilst for cyclopentane and cyclohexane the observed and calculated values are in satisfactory agreement. It is supposed that this corresponds with the stability of the various ring systems.

The data for benzene and its derivatives indicate that these are saturated compounds, whilst cyclohexadiene and cyclohexene behave like unsaturated hydrocarbons. The fact that benzene behaves like a saturated hydrocarbon on combustion is discussed

with reference to the question of its constitution. Since no double bonds are present, it is suggested that the unsaturation is distributed uniformly between all the carbon atoms in the molecule as represented by the formula



H. M. D.

Calculation of Constants for the Heats of Combustion of Hydrocarbons. H. STANLEY REDGROVE (*Chem. News*, 1914, 110, 73-74).—Polemical. The method of procedure, adopted by Le Bas (preceding abstract) in deducing constants from the heats of combustion of the hydrocarbons, is subjected to criticism. The relation between the heat of combustion of the saturated hydrocarbons and the valency number, according to which the constant for carbon is exactly four times the constant for hydrogen, is, in the author's opinion, accidental in character. If a general relationship were involved, it would hold for compounds containing other elements, which is not the case.

H. M. D.

Heat of Vaporisation of Normal Liquids. JAMES KENDALL (*J. Amer. Chem. Soc.*, 1914, 36, 1620-1630).—The accuracy of the various equations which have been proposed for representing the variation of heat of vaporisation with temperature has been tested by comparison with the experimental results obtained for octane, methyl butyrate, carbon tetrachloride, and fluorobenzene by Young. For the first three compounds, the author's equation (this vol., ii, 101) and that of Mills (*A.*, 1907, ii, 226) show the best agreement with Young's figures, whilst in the case of fluorobenzene the experimental results are shown to be inaccurate.

It is pointed out that no conclusions can be drawn as to the relative theoretical merits of the different formulæ, and that at present they are merely of service as checks on the experimental data.

E. G.

Influence of Temperature on the Density and Electrical Conductivity of Aqueous Salt Solutions. II. HEINRICH CLAUSEN (*Ann. Physik*, 1914, [iv], 44, 1067-1076. Compare *A.*, 1912, ii, 119).—The density and electrical conductivity of aqueous solutions of rubidium chloride, bromide, iodide, nitrate, and sulphate, and also of cesium chloride, have been measured at 6°, 18°, and 30°. The experimental data are interpreted in accordance with the views put forward by Heydweiller (*A.*, 1910, ii, 106; 1912, ii, 433), and afford further support for the theory that the difference in the density of solution and solvent is determined by coefficients characteristic of the ionised and non-ionised molecules.

H. M. D.

Electrical Conductivity and Viscosity of Solutions of Sodium Iodide and Potassium Iodide in Mixtures of Ethyl Alcohol and Water. E. P. WIGHTMAN, P. B. DAVIS, A. HOLMES, and HARRY C. JONES (*J. Chim. phys.*, 1914, 12, 385—427).—The viscosity and fluidity of $N/8$ -solutions of sodium iodide and potassium iodide in ethyl alcohol, and in mixtures of ethyl alcohol and water from 100—0%, have been determined at temperatures 15°, 25°, and 35°. Conductivity determinations have been made of $N/8$ - and $N/128$ -solutions of potassium iodide in alcohol-water mixtures from 0·0—96·09% alcohol at 20°, and a further series of $N/8$, $N/32$, $N/128$, and $N/1024$ in similar alcohol-water mixtures at the same temperature. There is a slight increase in the viscosity of alcohol-water mixtures when sodium iodide or potassium iodide is dissolved in them to form a $N/8$ -solution in all cases from 100% alcohol to 60% alcohol; below this concentration there is a slight diminution in the viscosity. On elevation of temperature, the point where the fluidity curve of the solution cuts that of the solvent is displaced, and the displacement is to be attributed to a change in the association of the solvent. The change in the association is greater for water than for alcohol. The viscosity changes are to be explained by the theory previously put forward by Jones and his collaborators (A., 1906, ii, 737). A continuous diminution in the electrical conductivity of solutions of potassium iodide and sodium iodide occurs on passing from pure water to pure alcohol, the diminution being most noticeable in those solutions containing a high percentage of water, and least noticeable in those containing a small percentage of water. This is probably to be explained by the fact that the association of alcohol is changed only very slightly by the addition of small quantities of water, whilst the association of water is strongly affected by the addition of small quantities of alcohol. Since viscosity and association are closely connected, it is to be taken that the same explanation will apply to the viscosity changes, or, to express it differently, in mixtures of alcohol and water there is a far larger change in the viscosity of the water than in that of the alcohol. The decrease in the conductivity of potassium iodide with increase in the percentage of alcohol is more rapid than the corresponding decrease for sodium iodide in the same solvents, due, no doubt, to the greater atomic volume of the potassium iodide (compare Jones and Veazey, A., 1907, ii, 438; 1908, ii, 259, 260). Hydration has practically no influence on the conductivity at any temperature, however; with the elevation of temperature the dissociation of feebly hydrated ions produces a slight increase in the temperature-coefficient of most solutions containing water. Alcohol solutions have temperature-coefficients which are linear functions, and consequently indicate that no "alcoholation" has occurred. The conductivity curves, which appear to be non-symmetrical, become symmetrical if they are prolonged up to 100%, and then they form symmetrical curves with the point of symmetry at 80% alcohol instead of 50%. On raising the temperature, the curves tend to become linear functions, which is to be attributed to the fact that

under similar conditions the fluidity curves also tend to become linear.

J. F. S.

Stalagmometric Estimations of Small Hydroxyl Ion Concentrations. JULIUS GRÖH and IRENE D. GÖTZ (*Biochem. Zeitsch.*, 1914, **66**, 165—172).—By means of a Donnan stalagmometer, the surface tension at the interface of a solution of 0.25% stearic acid and aqueous solutions of alkalis was measured. It was found that a calibration curve could be obtained for concentrations of pure sodium hydroxide solutions between the concentrations $2 \cdot 10^{-4}$ and $25 \cdot 10^{-4}$ *N*. The method is more sensitive when the alkaline solution contains neutral salts (for example, potassium chloride in about 0.3*N* concentration). In this case measurements could be made over the range of $5 \cdot 10^{-5}$ to $6 \cdot 10^{-4}$ *N*. The method is still more sensitive when the hydroxyl ions arise from the hydrolytic dissociation of weak salts, when concentrations of OH ions to $2 \cdot 10^{-7}$ *N* affect the tension at the interface. It was found, however, that it was not possible to employ the changes in the tensions at the interfaces to determine the hydrolysis constant, owing to disturbing influences (possibly adsorption phenomena).

S. B. S.

Stalagmometric Studies of Solutions of Colloids and Crystalloids. V. The Relationship between Physiological and Physico-chemical Action of Neutral Salts. L. BERCZELLER (*Biochem. Zeitsch.*, 1914, **66**, 173—190).—Capillary-active substances, such as ethyl alcohol, phenol, thymol, menthol, camphor, quinol, anaphthol, sodium glycocholate, albumose, and caseinogen, lower the surface tension of water more in the presence than in the absence of salts when the solutions are not saturated with the substances. These phenomena run parallel with the physiological activities of the substances. The surface tensions of the salt solutions saturated with these substances are, however, not smaller than those of the salt-free solutions. The surface tension of saturated ammonium sulphate solution is not lowered by thymol, camphor, menthol, or glycocholic acid. The various phenomena are best explained on the assumption of hydrate formation by salts.

S. B. S.

Stalagmometric Studies of Solutions of Colloids and Crystalloids. VI. The Action of Phenol on the Surface Tension of Protein Solutions. L. BERCZELLER (*Biochem. Zeitsch.*, 1914, **66**, 191—201).—The surface tension of solutions of serum, various proteins, peptones, and ereptone are lowered more by phenol than is that of pure water. The same phenomenon is shown by *p*-cresol and chloral hydrate, but not by ethyl alcohol, propyl alcohol, triacetin, and camphor. This lowering is not caused by the concentration at the surface of the phenol, but by that of the protein. The diminution of the bactericidal activity of phenol by serum, as observed by Ehrlich and Bechhold, can be explained by means of the surface-tension theory.

S. B. S.

Stalagmometric Studies of Solutions of Colloids and Crystalloids. VII. Pharmacological Activity and the Lowering of Surface Tensions. L. BERGZELLER (*Biochem. Zeitsch.*, 1914, 66, 202—206).—The measurements of the surface tensions of a number of phenol solutions show the general relationship between the capacity of substances to lower the surface tension of water and their pharmacological action as indicated by Traube and others. S. B. S.

Stalagmometric Studies of Solutions of Colloids and Crystalloids. VIII. Some Complexes of Protein and Starch with other Colloids. L. BERGZELLER (*Biochem. Zeitsch.*, 1914, 66, 207—217).—Soaps diminish the surface tension of water less in the presence of proteins than in their absence. The effect of the proteins is increased if the mixtures are kept some time before the stalagmometric measurements are made. Similar phenomena were observed with starch solutions, and with mixtures of albumoses and peptones with proteins. The results are explained on the assumption of the formation of colloidal complexes. Bile salts are bound by proteins, but not by starch. S. B. S.

Stalagmometric Studies of Solutions of Colloids and Crystalloids. IX. Colloidal Complexes of Cholesterol. L. BERGZELLER (*Biochem. Zeitsch.*, 1914, 66, 218—224).—The stalagmometric measurements indicate the formation of colloidal complexes in soap-cholesterol and soap-protein mixtures, which change with changing hydroxyl ion concentration. A complex, but not quite similar to these, is formed with lecithin and cholesterol. No evidence of a complex between saponin and cholesterol could be obtained. S. B. S.

Stalagmometric Studies of Solutions of Colloids and Crystalloids. X. The Action of Certain Narcotics on Lecithin Solutions. L. BERGZELLER (*Biochem. Zeitsch.*, 1914, 66, 225—230).—Narcotics increase the surface tension of lecithin solutions. After narcosis, the surface tension of the urine is often lowered by non-volatile products. S. B. S.

The Adsorption Isotherm in the Region of very Small Concentrations. G. TRÜMPER (*Kolloid. Zeitsch.*, 1914, 15, 10—18).—The question of the validity of the exponential adsorption formula at very small concentrations has been examined by experiments on the adsorption of fluorescein from aqueous solution by animal charcoal. The concentration of the fluorescein was determined spectrophotometrically in the case of the more concentrated solutions (0.05—0.0005 gram per litre), and by measurement of the intensity of the fluorescence in the case of the more dilute solutions (0.0005—0.000005 gram per litre).

From observations on the rate of adsorption, it was found that the initial stage in which the fluorescein is rapidly absorbed is succeeded by a period of relatively slow fall in the concentration

of the fluorescein solution. No definite condition of equilibrium was attainable, and on this account the experiments were arranged so as to afford a measure of the initial rapid absorption. This method of procedure is justified by the probability that the slow absorption is due to a secondary change not directly connected with the true adsorption.

The experimental results are in satisfactory agreement with the requirements of the formula $x = a \cdot c^n$ if $a = 0.25$ and $n = 0.18$. It would thus appear that there is no measurable lower limit of concentration at which the exponential formula loses its validity as a means of expressing the adsorption from solution. H. M. D.

Dissociation of Hydrogen into Atoms. I. IRVING LANGMUIR and G. M. J. MACKAY (*J. Amer. Chem. Soc.*, 1914 36, 1708—1722).—In earlier papers (A., 1912, ii, 231, 826, 1162) it has been shown that hydrogen, particularly at low pressures, is readily dissociated into atoms by metallic wires at very high temperatures. It has now been found, however, that there is good reason for suspecting that the actual values recorded for the degree of dissociation are much too high, and this was thought to be due to an incorrect assumption as to the diffusion-coefficient of hydrogen atoms through molecular hydrogen.

Experiments have therefore been carried out by methods which do not necessitate any assumption as to the magnitude of the diffusion-coefficient. Single-loop filaments of pure tungsten wire were mounted in large, cylindrical lamp-bulbs. The temperatures were determined by means of the relation $T = 11230/7.029 - \log H$, where H is the intrinsic brilliancy of the filament in international candle-power per sq. cm. of projected area. On this scale, the m. p. of tungsten is 3540° (abs. temp.), which is regarded as more probable than the lower values usually assigned to it. The temperatures were also determined by measuring the resistance, and also by matching the colour of the emitted light against that of a standard provided with a blue screen. The three methods nearly always gave concordant results.

Measurements have been made of the total losses of heat from tungsten wires in hydrogen at pressures ranging from 10 mm. up to ordinary atmospheric pressure, and also at very low pressures from 0.01 to 0.2 mm. Experiments have also been made with nitrogen in order to compare the loss of heat in this gas with that in hydrogen.

The results obtained show a striking difference in the effects in the two gases. In the case of nitrogen, the values for the power consumption decrease steadily at all temperatures as the pressure is reduced, and in hydrogen at temperatures up to $1500-1700^\circ$ a similar decrease occurs. At higher temperatures in hydrogen, however, the power consumption is much greater at low pressures than at atmospheric pressure. At very high temperatures, that part of the loss of heat which depends on the dissociation of the hydrogen increases very rapidly, and becomes 50 or 100 times as large as the possible experimental error.

E. G.

Osmotic Data in Relation to Progressive Hydration. W. R. BOUSFIELD (*Proc. Roy. Soc.*, 1914, [A], 90, 544—548).—A theoretical paper in which it is shown that the formula connecting the osmotic pressure with the vapour-pressure lowering of a solution may be deduced on the basis of a definition of osmotic pressure which does not permit of the assumption that this varies with hydrostatic pressure. The expressions given previously for the osmotic data in terms of progressive hydration (T., 1914, 105, 609) can now be written in the simpler and more accurate form

$$P/R'T = \Delta/F' = \delta p/p = i/h - n,$$

in which P is the osmotic pressure in atmospheres, Δ the freezing-point lowering, $\delta p/p$ the relative lowering of the vapour pressure, h the total number of molecules of water per molecule of solute, n the number of molecules of water combined with one molecule of solute, and i is the ionisation factor. The values of the constants are $R' = 4.557$ and $F' = 103.6$.
H. M. D.

Attempt at a Physical Explanation of the Semipermeability of Living Cells to Ions. PIERRE GIBARD (*Compt. rend.*, 1914, 159, 376—379).—If between an acid solution of barium chloride and pure water, each containing an electrode, a goldbeater skin 0.1 mm. in thickness intervenes, chlorine diffuses through into the water five times faster than the barium. If, on the other hand, an alkaline solution of barium chloride is used, it is the barium which diffuses the faster. If the thickness of the membrane is increased to 0.5 mm., the passage of the two ions equalise one another. In the system electrode-acid solution of barium chloride-water-electrode, the algebraic sum of the differences of potential is equal to +0.075 volt. The interposition of the thin membrane between the water and the barium chloride inverts the sign of the sum of the potential differences, and it becomes equal to -0.025 volt, this inversion favouring the passage of the chlorine ions. The author considers that it is this state of polarisation of the membrane which gives it its relative semipermeability, this being relative only on account of the progressive lowering of the state of polarisation. He is of the opinion that the above process is analogous to that which takes place in living cells. W. G.

The Most Simple Method of Crystallographic Description. E. VON FEDEROV (*Zeitsch. Kryst. Min.*, 1914, 54, 17—45).—For many years the author has been endeavouring to perfect a system whereby the crystalline form of a substance may be made to serve for its identification. In the course of this work, the difficulties incidental to the measurement of crystals, and the recording of the data necessary for their complete description, have been reduced to a minimum. The usual method of describing crystals is held to be very inconvenient, and such descriptions often contain numerous errors.

A special universal goniometer, designed for rapid rather than specially accurate work, is described. The necessary angles are measured with this instrument, and from them a goniostereo-

graphic projection is made upon a specially prepared diagram. By the method of zonal calculation, involving the employment of bipolar spherical co-ordinates, all other angles on the crystal can be calculated by simple addition or subtraction of natural co-tangents. The author appeals to crystallographers to employ his method of description in order to facilitate the tabulation of data for his tables for crystallochemical analysis. E. H. R.

The Theoretical and Experimental Investigation of Crystal Structure. P. GROTH (*Zeitsch. Kryst. Min.*, 1914, 54, 65—73).—A historical sketch of the development of the modern theory of crystal structure is given, followed by a description of the recent work of W. H. Bragg and W. L. Bragg, and a discussion of their results. It must now be concluded that molecules as such do not exist in crystals, but only in amorphous substances. Barlow and Pope came to the same conclusion in an entirely different manner. Polymorphism can no longer be explained by the difference in size between the molecules of the two modifications. Among other important questions which now arise is that of the difference between chemical and physical isomerides. In future, the "topic parameters" will be replaced by the actual dimensions of the space-unit of the crystal. E. H. R.

Chemical Significance of Crystalline Form. WILLIAM BARLOW and WILLIAM JACKSON POPE (*J. Amer. Chem. Soc.*, 1914, 36, 1675—1686, 1694—1695).—The authors reply to the objections raised by Richards (A., 1913, ii, 483) to their views on the relationship between crystal structure and chemical constitution, and point out that their method of quantitative treatment for the elucidation of this relationship has proved so fertile in co-ordinating chemistry and crystallography as to be incapable of being affected by such adverse criticism. E. G.

Further Remarks Concerning the Chemical Significance of Crystalline Form. THEODORE W. RICHARDS (*J. Amer. Chem. Soc.*, 1914, 36, 1686—1694).—A reply to Barlow and Pope (preceding abstract). E. G.

An Association of Crystals of Unlike Symmetry. A. DUFPOUR (*Compt. rend.*, 1914, 159, 260—263).—A study of mixed crystals of the isodimorphous dichromates of potassium and ammonium. From solutions containing less than 65% of ammonium salt, triclinic crystals, similar to those of the potassium salt, separate; when this proportion is exceeded, monoclinic crystals are formed, isomorphous with the ammonium salt, together with an unstable form of the potassium salt. From a solution containing 60% of ammonium dichromate, monoclinic crystals are first deposited. Subsequently, triclinic crystals grow upon the former, which themselves gradually disappear. From the regular manner in which the triclinic crystals become orientated upon the monoclinic variety, the author is led to modify the axial ratios of the

triclinic potassium salt. There is now seen to be a close morphotropic resemblance between the two kinds of crystal, which would account for the regular manner of growth of the one upon the other.

E. H. R.

Mixed Crystals of Ammonium Chloride with Manganese Chloride. H. W. FOOTE and BLAIR SAXTON (*J. Amer. Chem. Soc.*, 1914, **36**, 1695—1704).—Although several investigators have studied the products which are formed when mixed solutions of ammonium and manganese chlorides are allowed to crystallise, the extent of mixed crystal formation and the conditions under which mixed crystals are produced instead of double salts have not hitherto been determined.

A study of this subject has now been carried out by the solubility method employed by Foote (A., 1912, ii, 847) in investigating the mixed crystals of ammonium chloride with nickel and cobalt chlorides. Determinations have been made of the solubility of various mixtures of ammonium and manganese chlorides at 25°, and both the residues and solutions have been analysed.

The results show that ammonium chloride and the double salt $2\text{NH}_4\text{Cl} \cdot \text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ (Saunders, A., 1892, 781) form two series of mixed crystals, α and β , there being a gap between the limiting composition of each type. An investigation of the heats of formation of the mixed crystals has shown that that of the β -crystals is positive, whilst that of the α -crystals is negative. The β -crystals are to be regarded as a solid solution of ammonium chloride in the double salt, and the α -crystals as a solid solution of the double salt in ammonium chloride.

E. G.

Reversible Transformation of Emulsoid Solutions of Gum Arabic and Gelatin into the Suspensoid Condition and the Properties of these Systems. O. SCARPA (*Kolloid. Zeitsch.*, 1914, **15**, 8—10).—When ethyl alcohol is added gradually to an aqueous solution containing about 2% of gum arabic or gelatin, the liquid becomes opalescent, and ultramicroscopic observation indicates that the emulsoid has been transformed into a suspensoid. The change in question is reversible.

The colloidal particles of the suspensoid system move towards the positive pole in an electrical field, indicating that both gum arabic and gelatin are electro-negative colloids. The suspensoid solution of gum arabic is coagulated on the addition of most salts, acids, and bases, but a perfectly clear, non-opalescent solution is obtained by the addition of mercuric chloride. The opalescent solutions of gelatin are precipitated by mercuric chloride, copper sulphate, and ferric chloride, but most other electrolytes convert the suspensoid into an optically clear solution. The coagulation is in most cases reversible, and this holds also for the product which separates at the positive pole when an electric field is applied.

H. M. D.

Adsorption, Imbibition, and Osmotic Pressure of Colloids. M. POLÁNYI (*Biochem. Zeitsch.*, 1914, **66**, 258—268).—By means of a

thermodynamic cycle, the following relationships were deduced. When a gel is in equilibrium with a solution, $u = c/RT \cdot d\pi/dc$, where u is the amount of the dissolved substance concentrated in the gel, c the concentration of the solution, π the imbibition pressure of the gel, and R and T have the ordinary significance. The statement that has often been made, but not verified, that substances which favour imbibition are positively adsorbed, whereas those which inhibit imbibition are negatively adsorbed, is a strict law if certain premises are made. Such premises are fulfilled when the separation of the adsorbed substance can take place continuously, and the adsorption process is a reversible one. Accepting the same premises, substances which increase the osmotic pressure of colloids are positively adsorbed by the colloids, whereas those which diminish the osmotic pressure are negatively adsorbed. The following equation expresses the relation of a colloid to the solution, $u' = c/RT \cdot dp/dc$, where u' is the concentration of the substance in the colloid and p the osmotic pressure of the colloidal solution.

S. B. S.

Contraction Phenomena. RAPHAEL ED. LIESEGANG (*Kolloid. Zeitsch.*, 1914, 15, 18—23).—An account is given of a number of peculiar structures, the development of which is attributed to the contraction in gels and other systems in which chemical interaction is accompanied by the formation of precipitation membranes. The formation of completely enclosed cavities and of cavities communicating with the exterior may result in this way, and the importance of these effects in the interpretation of certain geological configurations is emphasised.

H. M. D.

Reversible Reactions of Water on Iron and Ferrous Oxide. G. CHAUDRON (*Compt. rend.*, 1914, 159, 237—239. Compare Sainte-Claire Deville, *ibid.*, 1870, 70, 105; Preuner, A., 1904, ii, 317).—A study of the equilibrium between iron and water at temperatures between 300° and 1000°. An apparatus similar in principle to that of Sainte-Claire Deville's (*loc. cit.*) was used, the source of heat being an electric furnace. The equilibrium was determined for the system iron, water, hydrogen, ferrous oxide, and for the system ferrous oxide, water, hydrogen, magnetic oxide of iron. There are two series of equilibria: (1) iron and ferrous oxide; (2) ferrous oxide and magnetic oxide of iron.

W. G.

Mechanism of Irreversible Phenomena Deduced from the Boltzmann-Gibbs Law of Distribution. R. MARCELLIN (*J. Chim. phys.*, 1914, 12, 451—460).—A theoretical paper in which results deduced by another method (A., 1911, ii, 27) are now obtained from the law of distribution of Boltzmann-Gibbs. It is shown (1) that a physico-chemical complex in process of transformation is made up of two systems which are changing in opposite directions, and consist of a system I, the mass of which is constantly increasing, and a system II, the mass of which is constantly decreasing. The velocity of change which is observed experiment-

ally is the resultant of these two changes, and is given by the formula $V = M[\exp(-A_1/RT) - \exp(-A_2/RT)]$, in which M is a constant depending on the temperature and the nature of the substance of the reacting system, A_1 and A_2 are respectively the affinities of the systems I and II, and V is the velocity at the time t . The velocity with which the opposing systems are destroyed is given as a function of the temperature by the expression $d \log_e v / dT = A/RT^2 + \alpha/RT + \beta/R$; in which the constants α and β are small in comparison with A . From the fact that a reaction does not take place instantaneously, the conclusion is to be drawn that the molecules capable of transformation are in an exceptional condition (critical condition), which is different from the mean condition. The energy necessary for converting a molecule in the mean condition into one in the critical condition is given by the expression $E = RT^2 \cdot d \log_e v / dT$. J. F. S.

Velocity of Catalysis of Butyric Acid by means of Thoria. A. KOEHLER (*Bull. Soc. chim.*, 1914. [iv]. 15, 649—657).—A study of the conditions governing the catalytic influence of thorium oxide on the conversion of butyric acid into butyrene by heat, the catalyst being distributed on the surface of glass balls in a copper tube. The results show that the amount of acid converted into ketone in a given time by a given weight of thorium oxide is constant and independent of the velocity of flow of the acid vapour. The velocity of decomposition is also independent of the weight of the catalyst used, the surface being constant, but it is apparently a function of the surface offered by the catalyst, and is probably proportional to this surface. The velocity of decomposition diminishes on diluting the acid with an inert vapour, when this dilution passes a certain limit. W. G.

The Question of Associate Atoms. F. H. LORING (*Chem. News*, 1914, 110, 25—26).—It is supposed that the atoms of certain elements, the atomic weights of which seem to be invariable, are in reality composite, and contain two or more associate atoms in perfectly definite proportions. H. M. D.

Theory of Valency and Molecular Structure. WILLIAM C. ANSEM (*J. Amer. Chem. Soc.*, 1914, 36, 1655—1675).—The theory put forward in this paper is based on the conception of molecules and atoms as systems of moving electrons, and of valency as a consequence of the relative stability of these systems. For example, a binary molecule composed of two univalent atoms is regarded as a stable system formed of two systems of moving electrons, the dynamic equilibrium being such that one electron oscillates periodically from one system to the other, and is common to both systems, neither of which is complete in itself. The oscillating electron is termed the "valence electron." Valency is thus the property or power which an atom possesses of sharing a certain number of electrons with one or more other atoms in such a way that the atoms so united form a complete or perfect electron-system.

which is electrically neutral. This theory is developed and applied to the explanation of the mechanism of chemical reactions, tautomerism, conductivity of metals, association, and dissociation and conductivity in electrolytes and gases.

E. G.

An Efficient Stirring Apparatus. WILHELM GLUUD and RICHARD KEMPF (*J. Soc. Chem. Ind.*, 1914, 33, 680).—The aim of the construction is to meet as many needs as possible with one apparatus. It consists of a flask of 1500 c.c. capacity, constricted somewhat at the base so as to be equally efficient for small quantities of liquid. It is fitted with a hollow, ground-glass stopper, through which the stirring rod passes, with a condenser, and with a dropping funnel. The absence of rubber stoppers makes it suitable for nitrations, etc., and the whole apparatus may be heated in an oil bath without risk of fracture. A pear-shaped trap, which is filled with paraffin oil or other suitable liquid, is fused on to the stirring rod in the flask, and an extension of the stopper dips into it, so as to seal off the interior of the flask from the metal fittings of the stopper and upper portion of the stirring rod. The apparatus is easily detachable for cleaning purposes.

G. F. M.

Inorganic Chemistry.

Bromine Hydrate. H. GRAN (*Compt. rend.*, 1914, 159, 246–248. Compare Löwig, *Ann. Phys. Chem.*, 1829, 16, 376; Roozeboom, A., 1886, 177).—A thermal analysis of mixtures of bromine and water containing more or less bromine than suffices to saturate the water, points to the composition of the hydrate of bromine being $\text{Br}_2 \cdot 8\text{H}_2\text{O}$, and this formula is confirmed by chemical analysis of a specimen of the hydrate carefully freed from any occluded bromine or water, by centrifuging it on kaolin at a temperature just above 0° .

W. G.

A New Method of Determining the Atomic Weight of Iodine. MARCEL GUICHARD (*Compt. rend.*, 1914, 159, 185–188).—The author has determined the atomic weight of iodine by weighing the iodine and oxygen liberated from a given weight of iodic anhydride on decomposition by heat. The iodic anhydride was prepared by the action of carefully purified, fuming nitric acid on iodine, and the product freed from occluded gases by heating at 330° , repeatedly crystallised, and finally dehydrated by heating in a vacuum at 240° for fifteen hours in the final decomposition tube. The iodine liberated in the estimation was condensed in a spiral tube 1 metre long, and the oxygen absorbed by carefully purified heated copper, the decomposition being regulated so that not more

than 6 grams of iodic anhydride were decomposed in five hours. All starting materials and end products were weighed in sealed, evacuated tubes. The mean of five determinations gave 126.915 as the atomic weight of iodine. W. G.

Nitrogen Generator. CHAR. VAN BRUNT (*J. Amer. Chem. Soc.*, 1914, **36**, 1448—1450).—The apparatus consists of a bulb provided with a long stem and a side-tube, and partly filled with an ammoniacal solution of ammonium carbonate or chloride; a tube filled with copper shavings is fitted into the top of the bulb. The stem of the latter is connected with a tube rising to the height of the bulb, and on this tube is a side-tube which extends upwards and enters the tube containing the copper shavings. A current of air is forced into the tube connected with the stem of the bulb, and rises upwards through the side-tube, carrying with it bubbles of the ammoniacal solution; the latter is thus circulated continuously and allowed to pass through the copper shavings, whilst the air, deprived of oxygen, collects in the upper part of the bulb and escapes through the side-tube of the latter. W. P. S.

Active Nitrogen. H. B. BAKER, ERICH TIEDE, R. J. STRUTT, and EMIL DOMCKE (*Ber.*, 1914, **47**, 2283—2284).—The contradictory results of Tiede and Domcke (*A.*, 1913, ii, 210; this vol., ii, 196) and Baker and Strutt (this vol., ii, 357) are due to differences in the apparatus employed. With the apparatus of the former investigators it was possible to increase the brightness of the after-glow of the electric discharge in nitrogen by the introduction of a little oxygen, a slightly larger quantity of oxygen, however, causing an entire disappearance of the effect. On the other hand, with the apparatus employed by the latter investigators, no appreciable diminution in the after-glow was observed even with pure nitrogen which gave the desired effect in the other apparatus.

It is therefore probable that a trace of oxygen favours those conditions in the discharge which give rise to active nitrogen, but in a suitable apparatus the result can be obtained even with the purest nitrogen. D. F. T.

The Nitrogen After-glow. Nitrogen Glow and Metallic Vapour. ERICH TIEDE and EMIL DOMCKE (*Ber.*, 1914, **47**, 2284—2285).—A final reply to König and Elöd (this vol., ii, 266), rejecting the suggestion that to metallic vapours are to be attributed the effects in the after-glow of nitrogen, which the authors have ascribed to oxygen (compare Baker, Tiede, Strutt and Domcke, preceding abstract). D. F. T.

Preparation of Ammonia from Nitrogen and Hydrogen at High Pressure and Temperature in Presence of a Catalyst. NICOTEM CARO (*D.R.-P.* 272638).—In the preparation of ammonia by passing a mixture of hydrogen and nitrogen at high pressure and temperature over soda-lime, potash-lime, etc., containing metals of the iron group, the latter are conveniently replaced by

either titanium or vanadium, or both, these giving an equally high yield of ammonia and showing less sensitiveness towards impurities acting as contact-poisons.

T. H. P.

Manufacture of Readily Soluble, Stable Perborate Preparations. VEREINIGTE FABRIKEN FÜR LABORATORIUMSBEDARF (D.R.P. 271194).—The normal salts used in the original process (A., 1913, i, 1052) are replaced by the corresponding acid salts, these being mixed, in the dry or dissolved state, with perborate in such proportion that their acidity is not more than sufficient to neutralise one-half of either the alkali or base present in the perborate. The preparation of the complex perborates is facilitated and their consistency improved if the constituents are either mixed with water or aqueous alcohol and dried at a gentle heat, or fused on a water-bath, and thus partly or completely dehydrated.

T. H. P.

Carbon: its Molecular Structure and Mode of Oxidation.

MAURICE COPISAROW (*Mem. Manchester Phil. Soc.*, 1914, 58, No. x, 1—11).—Basing his arguments on the three assumptions that a carbon molecule contains a large number of atoms, that a carbon atom is always quadrivalent, and that carbon exists in three allotropic modifications, the author advances reasons for his opinions that polyatomic molecules of elements may be represented by constitutional formulæ in a similar manner to the molecules of compounds, and that polyatomic molecules, combining with one another and yielding, finally, single molecules, must either disintegrate before the reaction, or more probably form a complex or complexes which are stable or unstable, according to the conditions (compare Dixon, T., 1896, 69, 774; 1899, 75, 630; Rhead and Wheeler, T., 1910, 97, 2181; 1911, 99, 1140; 1913, 103, 461).

The arrangement of the atoms in a carbon molecule must be such that the atoms can rotate freely or form a partly rigid structure, or a completely rigid structure; these three cases are considered to correspond with amorphous carbon, graphite, and diamond respectively.

C. S.

The Formation of Carbon Monoxide During the Rapid Combustion of Carbon.

F. M. G. JOHNSON and D. MCINTOSH (*Trans. Roy. Soc. Canada*, 1913, 7, iii, 161—162).—Percentages of carbon monoxide varying from 6.2 to 8.9 have been found in the gases produced by the combustion of a mixture of carbon with excess of potassium chlorate, either in a vacuum or in air. Since the temperature of the combustion was only about 1000°, the presence of carbon monoxide is not due to thermal decomposition of the dioxide, and it is therefore held to confirm the view that the formation of the monoxide is the first stage in the combustion of carbon.

G. F. M.

Colloidal Silicon. R. ASTFALK and A. GUTBIER (*Kolloid. Zeitsch.*, 1914, 15, 23—27).—The authors have prepared colloidal silicon by reduction of silica by the action of magnesium, potassium, and

sodium. Magnesium and potassium give rise to products which yield colloidal solutions of different degrees of stability. According to the results of numerous experiments, these solutions may be divided into two groups, but it has not been found possible to determine the conditions which yield solutions belonging to the respective groups. Both series of solutions are readily coagulated by rise of temperature and by the addition of electrolytes. By dialysing the more stable solutions prepared by reduction with potassium, it was found possible to concentrate the colloidal solutions to some extent by evaporation over concentrated sulphuric acid. In this way, solutions containing approximately 0.05% of the disperse phase could be obtained.

The yellow solutions obtained from the product of the reaction with sodium are in some respects much more stable. They are readily dialysed, and can be concentrated over concentrated sulphuric acid without much coagulation; the solutions are, however, sensitive towards electrolytes.

H. M. D.

Attempts to Produce the Rare Gases by Electric Discharge.

THOMAS R. MERTON (*Proc. Roy. Soc.*, 1914, [A], 90, 549—553).—The question of the production of neon and helium by electric discharge in vacuum tubes has been further examined with an arrangement of apparatus which differs considerably from that employed either by Collie and Patterson (*T.*, 1913, 103, 419) or by Strutt (this vol., ii, 201). In the design of this apparatus, the most rigorous precautions were taken to ensure the exclusion of air. Hydrogen was admitted into the completely exhausted apparatus by heating a small, enclosed palladium tube, and after the passage of an induction-coil discharge, the residual gas was examined spectroscopically in a fine capillary tube attached to the apparatus. In some of the earlier experiments the residual gas showed the spectrum of argon, but this was found to be due to an exceedingly small, but continuous, leakage of air into the apparatus. When this was eliminated, no trace of argon, neon, or helium was observed after the passage of the discharge through hydrogen. Experiments with electrodes of aluminium, copper, nickel, silver, platinum, and palladium all gave negative results.

It is pointed out that in the previous experiments (*loc. cit.*) the diatomic impurities in the residual gas were removed by means of cooled charcoal, a process which would also have removed any argon present. It is probable that in those experiments in which the author found considerable quantities of argon, neon and helium would have been detected if the argon had been removed in this way.

The spectroscopic test for argon appears to be more delicate than that for neon, and since there is about a thousand times as much argon as neon in the atmosphere, it follows, therefore, from Strutt's estimate of the sensitiveness of the test for neon that a millionth of a c.c. of air might be sufficient for the detection of argon.

It is considered doubtful whether stopcocks can be relied on in dealing with quantities of gas of this order of magnitude.

H. M. D.

Attempts to Produce the Rare Gases by Electric Discharge. J. NORMAN COLLIE (*Proc. Roy. Soc.*, 1914, [A], 90, 554—556).—A series of experiments *is described in which finely powdered metallic uranium, previously heated to redness in a vacuum, was subjected to cathode-ray bombardment in a bulb tube, which was sealed on to the apparatus used by Merton (see preceding abstract). A small charcoal bulb, a hard glass tube containing copper and copper oxide, and a small bulb filled with phosphoric oxide, were also sealed on to this apparatus. In nearly all the experiments described, neon and helium could be readily detected in the residual gas after passing the discharge for ninety minutes. In one experiment, in which the coil, giving a 10-inch spark with a platinum break, was replaced by a larger coil with a mercury break, neither neon nor helium could, however, be detected in the residual gas.

Since in no case was argon found to be present except in very small amounts, the author considers that the neon and helium cannot possibly be attributed to air leakage.

H. M. D.

Crystallised Sodium Silicate. EDUARD JORDIS (*Chem. Zeit.*, 1914, 38, 922).—Crystallised sodium silicates with 6, 9, and about 10 H_2O had m. p. $62\cdot3^\circ$, $47\cdot2^\circ$, and $37\cdot2^\circ$, respectively. A compound with $10\text{H}_2\text{O}$ is, however, difficult to obtain pure, as it gradually changes into the salt with $9\text{H}_2\text{O}$. When sodium silicate is heated for some time at 100° , a salt with $1\cdot5\text{H}_2\text{O}$ is obtained. The salt with $9\text{H}_2\text{O}$ forms rhombic crystals, that with $6\text{H}_2\text{O}$ monoclinic crystals. When the hydrated salts are heated or dried in a desiccator, there is difficulty in determining whether the resulting salts are definite compounds or mixtures.

W. P. S.

The Gases Retained by Iodine and Silver. PH. A. GUYE and F. E. E. GERMANN (*Compt. rend.*, 1914, 159, 225—227).—Using their special apparatus for the estimation and analysis of small volumes of gases (compare this vol., ii, 740), the authors have determined the amount of gas evolved on heating 1 gram of silver with one and a-half times its weight of iodine, carefully purified and previously heated in a vacuum. Two samples of silver were used: (1) ordinary pure silver (99·8%); (2) extra pure silver (100·0%), prepared by melting silver in a quartz vessel, bubbling hydrogen through it, and leaving it to solidify in an atmosphere of hydrogen. Sample (1) yielded 0·17 c.c. of gas from 1 gram of silver, of which four-fifths was oxygen and one-fifth carbon monoxide. Sample (2) yielded 0·027 c.c. of gas from 1 gram of the metal, which was all carbon monoxide, and also water vapour equivalent to 0·01 c.c. of a perfect gas at 0° and 760 mm. The bubbling of hydrogen

through the silver had thus eliminated the whole of the oxygen, leaving the volume of carbon monoxide practically unaltered.

W. G.

The Absorption of Nitrogen by Calcium. RICHARD BRANDI (*Zeitsch. angew. Chem.*, 1914, 27, 424).—Contrary to statements in the literature, metallic calcium in the compact form is found to absorb nitrogen rapidly and almost quantitatively with formation of the nitride, Ca_3N_2 . Absorption commences at about 300° , and attains a maximum velocity at 440° . Above 650° it once more gradually falls off to zero, but commences again above the melting point of calcium. The nitride retains the form of the original piece of metal, but it can readily be converted into chestnut-brown powder.

G. F. M.

The Dehydration of Gypsum. C. GAUDEFEY (*Compt. rend.*, 1914, 159, 263–264).—The passage from the hemihydrate to the soluble form of anhydrous calcium sulphate at 120 – 130° is not accompanied by any change in form or size of the crystals. The anhydrous salt is, however, less refractive than, and has a birefractation almost double, that of the hemihydrate.

W. G.

Tellurium as Colouring Agent for Soda Glass. P. FENAROLI (*Chem. Zeit.*, 1914, 38, 873–874).—Tellurium, like selenium, in the oxidised state does not impart a colour to glass, but if elementary tellurium is added to an ordinary soda glass and fused under reducing conditions, for example, in the presence of charcoal, glasses are obtained of colours varying according to the amount of tellurium used. Some contain colloidal solutions of the element, and others polytellurides. The former correspond completely with the tellurium hydrosols, and are, like them, of two fundamental colours, blue and brown, analogous to the red selenium glass. The blue glass contains larger colloidal particles than the brown. The glass containing polytellurides is red, or violet-red, and has an absorption spectrum which corresponds exactly with that of aqueous solutions of polytellurides, showing an absorption from the green to the violet, with a distinct maximum between 480 and 490μ .

G. F. M.

Glucinum Sulphate and its Hydrates. F. TABOURY (*Compt. rend.*, 1914, 159, 180–182).—The progressive dehydration, by heating, of the tetrahydrate of glucinum sulphate confirms the existence of the di- and mono-hydrates, the former being obtained at 55 – 60° and the latter at 100° , and indicates the existence of a hemihydrate obtainable at 150 – 160° . The anhydrous salt obtained at 250° is stable up to 530 – 540° , and thus allows of the estimation of glucinum in the form of its sulphate. Glucinum sulphate does not form acid salts even when dissolved in sulphuric acid.

W. G.

The Corrosion of Metals by Water. A. T. STUART (*Trans. Roy. Soc. Canada*, 1913, 7, 183–188).—Comparisons have been made

of the relative corrosivity of "raw" Ottawa River water, and the same water which had been treated either by "mechanical filtration" or with alum or magnesia. The metals were employed in the form of wire, and were suspended in the water for seven days, some at ordinary temperatures and others at 60°. The corrosion was measured in terms of the loss in weight after the products of corrosion had been rubbed off with a cloth. In addition to the "pure" metals, the effect of couples of two unlike metals in contact was also studied. It was found that raw waters, although corroding iron to practically the same extent as treated waters, retained most of the product in colloidal solution, and did not coat the metal with as much flocculent material, nor allow it to settle out, as was the case with treated waters, which became very murky and opaque even at the ordinary temperature. A rise in temperature greatly accelerated the corrosion. The contact of aluminium with iron or with lead diminished the corrosion observed with the iron or lead alone, and increase in temperature produced a further decrease. Contact with copper caused exactly the reverse effects, and in the case of copper and lead an enormous increase of corrosion was observed. It was noticed that the iron wires carried a large number of tubercles, at the centre of which the metal was nearly eaten away. These were possibly the seats of colonies of iron-dissolving bacteria or algæ. Water treated for clarification with magnesium oxide had a considerably smaller corrosive action than the raw or otherwise treated water. This suggests the possible use of this substance as a pigment in anti-corrosive paint.

G. F. M.

Ternary Alloy, Zinc-Silver-Lead. B. BOGITCH (*Compt. rend.*, 1914, 159, 178—180).—On melting together lead, silver, and zinc, two layers are generally formed, and the author has studied the distribution of the three metals between the two layers at the temperature of solidification of the top layer, this being the poorer in lead, and consequently less fusible. Some twenty fused mixtures were studied, and a curve is given showing the proportions of the three metals which give two layers, and those which can exist without liquation. These results only hold good for temperatures near to the solidification point.

W. G.

The Reduction of the Oxides of Copper, Lead, and Nickel. PAUL SABATIER and LÉO ESPIL (*Compt. rend.*, 1914, 159, 137—142).—Copper oxide undergoes reduction by dry hydrogen at 120°. The curve showing the rate of reduction is formed by one branch only, the velocity being small at first, then increasing rapidly up to a certain point, after which it diminishes regularly. This oxide is reduced directly to the metal without the intermediate formation of cuprous oxide.

The reduction of lead peroxide by a stream of dry hydrogen is first manifest at 150°, it being reduced to the protoxide without the intermediate formation of red lead (compare Glaser, A., 1903, ii, 646). The protoxide, litharge, is first visible at 190°, it being

slowly transformed at this temperature, and more rapidly at 240° into the suboxide, Pb_2O , this oxide being, in its turn, slowly reduced to metallic lead at 250° , and rapidly at 300° .

The authors have repeated their work, already described (this vol., ii, 276), on the reduction of nickel oxide, and maintain their opinion that the unstable, intermediate suboxide formed has the constitution Ni_4O , and not Ni_2O as given by Berger (this vol., ii, 656). W. G.

The Chemical Composition of Alkaline Bordeaux Mixtures and the Soluble Copper which they Contain. V. VERMOREL and E. DANTON (*Compt. rend.*, 1914, 159, 266—268).—If concentrated milk of lime is poured rapidly into a dilute solution of copper sulphate, using an amount of lime such as to give 1 gram per litre in excess, a blue precipitate is formed, which consists mainly of Peligot's stable hydrated oxide, together with a little of the unstable hydrate and a small proportion of basic sulphates. On boiling, only a portion of this precipitate is dehydrated. On filtering off the precipitate, the filtrate is found to contain both copper and lime in solution. The copper is precipitated on boiling or by the passage of carbon dioxide, but dissolves in excess of this gas. The amount of copper in solution expressed as copper sulphate may amount to as much as 0.23 gram per litre. Using the same proportions, but pouring the milk of lime slowly into the copper sulphate solution, a green precipitate is formed, which consists almost entirely of basic sulphates, which are not affected by the presence of free lime, except on boiling the mixture. The filtrate from the green precipitate also contains both lime and copper in solution, the latter, expressed as copper sulphate, reaching as much as 0.41 gram per litre. W. G.

Simple Method for the Purification of Mercury. C. MARGOT (*Arch. Sci. phys. nat.*, 1914, [iv], 38, 46—52).—The method for the purification of mercury consists in placing the mercury in an inclined iron tube 160 cm. long and 3 cm. diameter. The tube is fitted with three vertical iron side-tubes, one at each end and one in the middle; the upper side-tube is connected through a Woulfe's bottle with a water pump, the lower side-tube is fitted with a funnel, and the tube in the centre carries a thermometer. The tube is heated midway between the lower and centre side-tubes by means of a Bunsen burner until the temperature has reached 150 — 160° , and then a current of air is drawn through. In this way a very rapid oxidation of the impurities is brought about, and any volatilised mercury is condensed in the Woulfe's bottle. By this means very dirty mercury can be completely purified in twenty-four hours. After the current of air has been stopped and the mercury allowed to cool, it is necessary to filter through fine linen to remove the oxides. With an apparatus of the dimensions stated above, about 12 kilos. of mercury can be treated at once.

J. F. S.

Isolation of Neoytterbium. J. BLUMENFELD and G. URBAIN (*Compt. rend.*, 1914, 159, 323—326).—The authors have submitted the earths of the ytterbium group, in the form of their nitrates, to a process of fractional crystallisation (compare Urbain, A., 1907, ii, 956; 1908, ii, 108), following the stages in the purification by measuring the coefficients of magnetisation of each fraction. After four thousand crystallisations they have obtained eight successive fractions having the same coefficient, indicating the isolation of a definite compound. The metal of the nitrate corresponding with these fractions they call "neoytterbium." The paramagnetism of its oxide is 33.6, and the atomic weight of the metal is 173.54. The spectra of these fractions show but very feebly the strongest rays of lutecium (compare Urbain, *loc. cit.*), or of thulium (compare Soret, A., 1880, 7, and Cleve, *ibid.*). The spectra do not contain the rays of aldebaranium, as indicated by Auer von Welsbach (compare this vol., ii, 130).
W. G.

Reversible Hydrosols Derived from Aluminium Hydroxide. R. PHILLIPS ROSE (*Koll. Chem. Beihefte*, 1914, 6, 1—7).—In the course of experiments on the adsorption of barium salts by precipitated aluminium hydroxide, it was found that a reversible gel was precipitated on the addition of hydrochloric acid to a solution of aluminium hydroxide in dilute acetic acid. The conditions which determine the formation of the sol and gel forms have been examined in detail.

Aluminium hydroxide, precipitated by the addition of ammonia to a solution of aluminium chloride or nitrate, varies very markedly in its solubility in dilute acetic acid (8%) according to the extent to which it is dehydrated. The hydroxide, dehydrated at low temperatures, yields the sol if its composition lies between $\text{Al}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$ and $\text{Al}_2\text{O}_3 \cdot 1.9\text{H}_2\text{O}$. The maximum amount of sol is formed when the composition is between $\text{Al}_2\text{O}_3 \cdot 4.5\text{H}_2\text{O}$ and $\text{Al}_2\text{O}_3 \cdot 3.7\text{H}_2\text{O}$. From experiments on the solubility of a hydroxide of the approximate composition $\text{Al}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ in acetic acid solutions of varying concentration, a maximum sol formation was found for solutions containing 6—8% of acid. Solutions of propionic, butyric, hydrochloric, hydrobromic, hydriodic, and nitric acid also gave rise to the sol, and the most favourable concentrations have been determined for each of these acids.

The sol is coagulated by the addition of aluminium salts, by hydrochloric and other acids, and this process is reversible. Irreversible coagulation occurs on the addition of potassium or sodium sulphate. The observations are discussed from a theoretical point of view.
H. M. D.

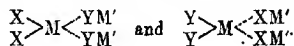
Iron-Zinc Alloys. F. TABOURY (*Compt. rend.*, 1914, 159, 241—243).—The author has examined the crystals which are formed in galvanising tanks, where the zinc is kept at a temperature slightly above its melting point for several months. He finds that they are identical with the mixed crystals containing 7.3% of

iron, as indicated by Vegesack (compare A., 1907, ii, 170). His determinations of the *E.M.F.* of the metal in which they are embedded agrees with the results obtained by Vigouroux, Ducelliez and Bourbon (A., 1912, ii, 648), the metal being zinc, and not an alloy of low iron content (compare Vegesack, *loc. cit.*). W. G.

Iron-Zinc Alloys. H. LE CHATELIER (*Compt. rend.*, 1914, 159, 356—357).—The author points out that Berthier (1840) and himself (1889) published the results of work on iron-zinc alloys far earlier than Vigouroux (A., 1912, ii, 648) or Vegesack (A., 1907, ii, 170), the only workers referred to by Taboury (compare preceding abstract). The author had proved the composition of the alloy to correspond with FeZn_{10} , and had shown that chromium gave a similar compound, CrZn_{10} . His results have been elaborated and confirmed by Wologdine (compare *Rev. Metal.*, 1906, 3, 701). The author does not consider that the measurements of *E.M.F.* permit of an exact determination of the formula of a chemical compound. W. G.

The Solid Chromic Sulphates. A. SÉNÉCHAL (*Compt. rend.*, 1914, 159, 243—246).—The author agrees with Colson (compare A., 1907, ii, 177) that the green chromium sulphate obtained by Recoura from the violet sulphate by heating it at 90° (compare A., 1896, ii, 27) has the composition $\text{Cr}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$. This dehydration commences in a dry vacuum at 30° , the salt gradually turning green, and being composed then of two phases. The green sulphate dissociates slowly in dry air at 80° , giving, finally, a new hydrate, $\text{Cr}_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$. All the substances of composition intermediate between this and the hexahydrate are soluble in water, their solubility diminishing with their water content. This trihydrate slowly loses water at 150° , but a temperature of 400° is necessary in order to obtain the anhydrous salt, this and the intermediate hydrates being insoluble even in boiling water. For the hydrates from $\text{Cr}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ to $\text{Cr}_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$ their molecular volume is an additive property, and can be calculated knowing the molecular volume of any one of them and of water in the solid state. The molecular volumes of the salts obtained by the dehydration of the trihydrate diminish more rapidly than would be the case if they followed a law of additivity. W. G.

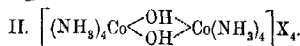
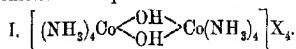
Neutralisation of the Affinity of Main and Subsidiary Valencies in Compounds of a Higher Order. J. V. DUBSKY (*J. pr. Chem.*, 1914, [ii], 90, 61—118).—According to Werner's original theory of main and subsidiary valencies, additive compounds of the general formula $\text{MX}_2 \cdot 2\text{M}'\text{Y}$, produced by the union of two different haloid salts, should exist in two isomeric forms,



Up to the present, however, no well-established instance of the existence of valency isomerides of this type has been recorded.

With the object of gaining further information on this point, the author has examined the additive compounds formed by the union of haloid salts of papaverine with cadmium and zinc haloids, but has failed to obtain any evidence of the existence of such isomerides. The additive compounds of papaverine hydrochloride, for example, with zinc and cadmium bromides, proved to be identical in solubility, melting point, crystalline form, and optical rotation with those obtained by the combination of papaverine hydrobromide with zinc and cadmium chlorides. These results thus confirm Werner's recent conclusion (this vol., i, 18) that there is no essential difference between main and subsidiary valencies.

Further evidence in support of Werner's view is furnished by the behaviour of octamminedioldicobaltic salts which are formed by the loss of water from two molecules of hydroxo-aqua-tetramminecobaltic salts, $[(\text{NH}_3)_4\text{Co} \begin{smallmatrix} \text{OH} \\ \diagup \diagdown \\ \text{OH} \end{smallmatrix}] \text{X}_2$, and, therefore, receive the symmetrical constitution I. On the other hand, the diol-salts are quantitatively resolved by the action of halogen acids into *cis*-diaqua-tetrammine- and *cis*-dihalogenotetrammine-cobaltic salts, a result which can only be satisfactorily interpreted on the assumption that the octamminedioldicobaltic salts have the unsymmetrical constitution represented in II.



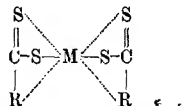
In view of the pronounced tendency of the acetato-group to enter into bridge-formation in multinuclear metallic complex salts, the behaviour of a number of ol-salts towards acetic anhydride has been studied.

Although hydroxopentamminecobaltic salts are readily converted into the corresponding acetato-salts by the action of acetic anhydride at the ordinary temperature, the dioldicobaltic and dioldichromic salts remain unchanged, even when heated for several hours with this reagent. Hydroxo-aqua-tetrammine salts, on the other hand, are quantitatively converted into diol-salts. Thus, hydroxo-aqua-diethylenediammine-cobaltic and -chromic salts, $[\text{en}_2 \text{M}(\text{OH})(\text{OH}_2)] \text{X}_2$, when warmed with acetic anhydride yield the corresponding tetraethylenediamminediol salts.

Attempts have been made to apply this method of preparing diol-salts to the preparation of heterogeneous dioldmetallic salts of the type $[\text{Y}_4\text{Co} \begin{smallmatrix} \text{OH} \\ \diagup \diagdown \\ \text{OH} \end{smallmatrix} \text{CrY}'_4] \text{X}_4$ (where Y_4 and $\text{Y}'_4 = 4\text{NH}_3$ or en_2) by the action of acetic anhydride on equimolecular proportions of hydroxo-aqua-tetrammine-cobaltic and -chromic salts. These attempts, however, were unsuccessful, a mixture of the octammine-dioldicobaltic and -dichromic salts being obtained.

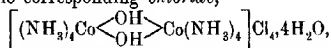
The author also discusses the constitution of the complex salts of chromium and iron with carboxylic acids, and gives an account of the preparation and properties of the ferric, chromic, and

cobaltic salts of xanthic acid. The xanthates exhibit the characteristic properties of internal complex salts, and are represented by the formula

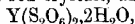


(R=OEt); a similar constitution is assigned to the salts of bi- and ter-valent metals with dithiocarbamic acid (R=NH₂) and its dialkyl derivatives.

When heated with acetic anhydride, hydroxo-aquo-tetrammine-cobaltisulphate is converted into octamminedioldicobaltisulphate, from which the corresponding chloride,

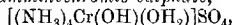


small, lustrous, dark ruby-red crystals, and dithionate,



lustrous, light violet crystals, were obtained by treatment with ammonium chloride and sodium dithionate respectively.

Hydroxo-aquo-tetramminechromic sulphate,



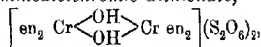
prepared by the addition of pyridine to an aqueous solution of chloro-aquo-tetramminechromic sulphate, forms violet-red crystals, and when heated with acetic anhydride is transformed into octamminedioldichromic sulphate, from which the bromide and dithionate, $\left[(\text{NH}_3)_4 \text{Cr} \begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{OH} \end{array} \text{Cr} (\text{NH}_3)_4 \right] (\text{S}_2\text{O}_6)_2 \cdot 4\text{H}_2\text{O}$ (Grodsenski,

Diss., Zürich, 1910), were obtained in the usual manner.

The action of acetic anhydride on both *cis*- and *trans*-hydroxo-aquodiethylenediamminecobaltic dithionate gives rise to the same tetraethylenediamminedioldicobaltic salts (Werner, *Annalen*, 1910, 375, 85). The following new salts of this series are described

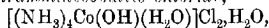
(Y = $\left[\text{en}_2 \text{Co} \begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{OH} \end{array} \text{Co} \text{en}_2 \right]$): dithionate, Y(S₂O₆)₂; chloride, YCl₄·4H₂O, lustrous, ruby-red crystals; and iodide, YI₄.

cis-Hydroxo-aquodiethylenediamminechromic dithionate yields tetraethylenediamminedioldichromic dithionate,



from which the following new salts were prepared: chloride, YCl₄·2H₂O, microscopic, dark bluish-violet crystals; thiocyanate, Y(SCN)₄; nitrate, Y(NO₃)₄·2H₂O; and chromate, Y(CrO₄)₂·4H₂O, brownish-red crystals.

Hydroxo-aquo-tetramminecobaltic chloride,



prepared by dissolving octamminedioldicobaltic chloride in strong aqueous ammonia, crystallises in slender, violet-red leaflets.

Hydroxopentamminechromic dithionate, $[(\text{NH}_3)_5 \text{Cr}(\text{OH})]\text{S}_2\text{O}_6$, separates with 2H₂O in carmine-red crystals, which decompose slowly at the ordinary temperature with evolution of ammonia;

when dissolved in acetic acid or treated with acetic anhydride at the ordinary temperature, it is converted into *aquopentamminechromic dithionate*, $[(\text{NH}_3)_5\text{Cr}(\text{OH}_2)]_2(\text{S}_2\text{O}_6)_3 \cdot 2\text{H}_2\text{O}$, which forms light, brownish-red crystals, and is reconverted into the hydroxo-salt on treatment with aqueous ammonia. When heated with acetic anhydride, the anhydrous hydroxo-salt undergoes decomposition.

Hydroxo-aquotetramminecobaltic sulphate, on solution in acetic acid, yields Jörgensen's diaquotetramminecobaltic sulphate, to which the author assigns the formula $[(\text{NH}_3)_4\text{Co}(\text{OH}_2)]_2(\text{O}_2\text{S})_3$, the latter compound loses $7\text{H}_2\text{O}$ at $110-120^\circ$, and passes into an intensely violet sulphatetetramminecobaltic salt. Unsuccessful attempts to prepare diol-salts by the action of acetic anhydride on dihydroxodiaquodiamminechromic bromide and hydroxo-aquodipyridinediamminecobaltic dithionate are also recorded.

Ferric benzenesulphonate, $[\text{Fe}(\text{OH}_2)_6](\text{C}_6\text{H}_5\text{SO}_3)_3 \cdot 3\text{H}_2\text{O}$, prepared from ferric hydroxide and an aqueous solution of the free acid or by the interaction of ferric sulphate and barium benzenesulphonate, crystallises from ethyl acetate in light yellow leaflets or plates, which sinter at 56° , melt at 60° to a turbid liquid, which becomes clear at 80° , and resolidifies at 160° .

Ferric benzenesulphinat, $\text{Fe}(\text{C}_6\text{H}_5\text{SO}_2)_3$, is obtained as a voluminous, orange-yellow precipitate by adding an alcoholic solution of benzenesulphinic acid to aqueous ferric chloride.

[With S. VRETOs.]—The additive compound of papaverine hydrochloride and cadmium bromide, $2\text{C}_{20}\text{H}_{27}\text{O}_4\text{N} \cdot 2\text{HCl} \cdot \text{CdBr}_2$, separates in lustrous, white, silky crystals when the two anhydrous salts are brought together in alcoholic solution. It becomes yellow at 100° , m. p. 185° , and is identical with the compound formed by the union of papaverine hydrobromide and cadmium chloride; if the components are not anhydrous, the additive compound separates in crystals containing $1\text{H}_2\text{O}$.

The following additive compounds were prepared in a similar manner ($\text{B} = \text{C}_{20}\text{H}_{27}\text{O}_4\text{N}$): $2\text{B} \cdot \text{H}_2\text{CdCl}_2\text{I}_2$, aggregates of slender leaflets, m. p. 176° ; $2\text{B} \cdot \text{H}_2\text{CdBr}_2\text{I}_2$, m. p. 188° ; $2\text{B} \cdot \text{H}_2\text{ZnCl}_2\text{Br}_2$, m. p. 177° .

Ferric xanthate, $\text{Fe}(\text{CS}_2\text{OEt})_3$, prepared from ferric chloride and potassium xanthate in aqueous solution, separates from carbon disulphide in small, brownish-black crystals. Its solution in pyridine, on dilution with water, deposits lustrous, golden-yellow leaflets, having the composition $\text{Fe}(\text{CS}_2\text{OEt})_3 \cdot 3\text{C}_5\text{NH}_5$.

The cobalt salt (small, blackish-green needles, m. p. 117°) and chromic salt (dark blue crystals) differ from the ferric salt in that they do not yield additive compounds with pyridine. All three xanthates give normal molecular weights in ethylene dibromide or benzene solution. F. B.

Reduction of Uranium Oxide. ERIC K. RIDEAL (*J. Soc. Chem. Ind.*, 1914, 33, 673—676).—In view of the increasing quantities of uranium salts produced as by-products, several

methods have been investigated which might be suitable for the industrial production of metallic uranium. From uranous salts, the best procedure was found to be the preparation of the tetrachloride by the action of chlorine on an intimate mixture of uranium dioxide and carbon heated at a low red heat, and the subsequent treatment of this substance with sodium and sodium chloride in a steel cylinder heated at 800° in a resistance furnace for forty-five minutes. A brown powder was obtained containing 99.3% of uranium. The electrolysis of uranium tetrachloride, using a mercury cathode, was also tried, but with unsatisfactory results, and the industrial preparation of uranium by either of these methods does not appear feasible. Several methods for the reduction of urano-uranic oxide, U_3O_8 , were investigated. Electrolysis in the solid state in an atmosphere of hydrogen gave under all conditions of pressure a black, crystalline product consisting of the dioxide, and a repetition of Stavenhagen's experiments, using magnesium or aluminium, yielded only a regulus of magnesia or alumina with the dioxide and unburnt metal. An electrothermal process, involving the use of magnesium powder, yielded, however, uranium of 98–99% purity. The oxide with 20% of magnesium was pressed into rods and placed in a tube of magnesia in contact with the carbon electrodes of an arc furnace. Hydrogen was passed through the apparatus, which was heated in a granular carbon resistor until the rods were hot enough to conduct the main current, which produced an arc of magnesium vapour, which effectively reduced the uranium oxide. The freshly prepared metal was spontaneously inflammable in air. Reduction of the oxide can also be effected by heating with magnesium and sodium in presence of calcium chloride as a catalyst, and an impure metal was obtained by Moissan's method of reducing with carbon in the arc furnace. The melting point of uranium containing 0.4% of carbon lay between 1300° and 1400° . G. F. M.

Removal of Iron from Oxygenated or Roasted Tin Sulphide Ores by Lixiviation with Acid. MARCO CHIAPPONI and ROBERT HESSE (D.R.-P. 271594).—The oxygenated ore is treated at 300 – 500° with a reducing agent, preferably gaseous in nature, so as to avoid introduction of impurities in the form of ash. Under these conditions the stannic oxide undergoes no, or but slight, reduction, and remains insoluble in acid, whereas the iron oxides are converted principally into ferrous oxide, which can be extracted readily by aqueous hydrochloric or sulphuric acid, or, better, by hydrogen chloride at 400 – 500° in a counter-current apparatus, the iron then distilling off as volatile chloride.

T. H. P.

Influence of Manganese Compounds on the Surface Alteration and Secondary Enrichment of Gold Deposits. W. H. EMMONS (*Zeitsch. Krist. Min.*, 1914, 54, 74; from *Trans. Amer. Inst. Min. Engin.*, 41, 768–837).—Ferric, manganic, and cupric salts present in natural waters, together with chlorides, liberate free chlorine, and gold may thereby be dissolved. It may

afterwards be deposited (principally by the agency of ferrous sulphate) in some other situation where there is no oxidation. Solutions containing 0.1% chloride, together with manganese, are capable of dissolving gold in the cold.

L. J. S.

Mineralogical Chemistry.

Organic Matter in Oil Shales. JOHN B. ROBERTSON (*Proc. Roy. Soc. Edin.*, 1914, **34**, 190—201).—The results of analysis of thirteen shales showed that the ratio C/H varies from 6 to 8 and above. The yield of oil from shales varies directly as the percentage of organic matter, and inversely as a function of the carbon-hydrogen ratio. In all the shales examined, the ratio C/H is lower than in ordinary bituminous coals. The richer varieties may, however, approach cannel coals in properties. The organic matter of oil-shales is mainly insoluble in organic solvents. From torbanite and Broxburn shale, pyridine dissolved 4.92 and 3.29% respectively of the ash-free dry substance; the amount of resinous substances present is therefore quite small.

By the action of concentrated nitric acid on some of the shales, acids were obtained of a similar nature to those obtained by Anderson from coal (*J. Soc. Chem. Ind.*, 1898, **17**, 1018). The acids form a series, beginning with lycopodium acid, in which the hydrogen is relatively highest, and ending with ordinary coal acids, in which it is relatively lowest. Torbanite, Broxburn shale, peat, and cannel coal yield intermediate acids in the order as given, and they probably represent different stages in the alteration of vegetable matter. There is no evidence of the presence of animal residues; phosphates could not be detected, and the amounts of lime in the ash varied from a trace to 1.55%. The conclusion is drawn that the organic matter is derived from algae, spores, or concretions of macerated organic material similar to that found in peat and cannel coal.

N. H. J. M.

Empressite, a New Silver-Tellurium Mineral from Colorado.

W. M. BRADLEY (*Amer. J. Sci.*, 1914, [iv], **38**, 163—165).—This mineral was found as finely granular masses with metallic lustre in the Empress-Josephine mine, Kerber Creek district, Colorado. On the small, conchoidal and uneven surfaces of fracture, the colour is pale bronze; the streak is greyish-black. The mineral is brittle to friable, and has H 3—3½, D 7.510. It is readily fusible, and is soluble in hot dilute nitric acid. Analysis agrees with the formula AgTe.

Ag.	Te.	Fe.	Insol.	Total.
45.17	54.75	0.22	0.39	100.53

L. J. S.

Bilinite, a New Bohemian Mineral. J. ŠEBOR (*Jahrb. Min.*, 1914, i, ref. 395—396; from *Sborník Klubu přírodovědeckého, Prag*, 1913, No. II, 2 p.).—A mineral resembling coquimbite occurs in a lignite mine at Schwaz, near Bilin. It is white to yellowish, with a fine, radially-fibrous structure. Hardness about 2, D 1·875. The optical characters resemble those of halotrichite, of which the new mineral is the iron analogue. Analysis I is of the surface material, and II from the interior:

	SO ₃	FeO	Fe ₂ O ₃	MgO	Na ₂ O	H ₂ O	Cl	Total
I.	32·80	5·86	15·95	0·04	0·90	39·82	2·11	97·48
II.	34·87	6·98	15·88	0·13	0·29	41·77	—	99·87

These give a formula $\text{Fe}''\text{Fe}'''_2\text{S}_4\text{O}_{16}\cdot 24\text{H}_2\text{O}$, analogous to that of halotrichite ($\text{Fe}''\text{Al}_2\text{S}_4\text{O}_{16}\cdot 24\text{H}_2\text{O}$). The mineral has been deposited from acid solutions resulting from the oxidation of pyrites.

L. J. S.

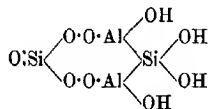
Precious Stones from Lower California, Mexico. ERNST WIRNICH (*Centr. Min.*, 1914, 449—456).—Pale rose-red lithia-tourmaline (rubellite), occurring in biotite-schist in the mountain ranges between Calamahí and San Borja, gave the following results on analysis:

SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	B ₂ O ₃	F
37·54	2·60	43·46	0·64	0·27	9·12	0·12
Li ₂ O	K ₂ O	Na ₂ O	H ₂ O	Total		
0·56	1·68	2·51	1·87	100·27		

Embedded in this rubellite are sometimes crystals of sapphire. Other gem-minerals described from Lower Californian localities include beryl, garnet (hessonite and spessartite), and turquoise.

L. J. S.

Chemical Structure of Kaolin. J. V. SAMOILOV (*Bull. Acad. Sci. St. Pétersbourg*, 1914, [vi], 8, i, 779—794).—The author has studied the heat effects observed when kaolin is heated in an electric furnace. From the results obtained, taken in conjunction with those given under similar conditions by opal, bauxite, diasporé, aluminium hydroxide, allophane, andalusite, disthène, and sillimanite, the conclusion is drawn that the two mols. of silica present in kaolin are differently combined with the alumina (compare Simmonds, T., 1903, 83, 1469). The structural formula



is proposed for kaolin. Complete removal of water is accompanied by resolution into silica and the silicate, Al_2SiO_5 . T. H. P.

Mineral Waters of Moncatini Owned by the Crown. R. GUARESCHI (*Ann. Chim. Applicata*, 1914, 1, 506—514).—These

waters exhibit ordinary physical and chemical characters, the temperature varying widely with the different springs, but being in all cases appreciably above that of the atmosphere. Their principal saline constituent is sodium chloride, which occurs, together with magnesium and potassium chlorides, sulphates of the alkali and alkaline-earth metals, and magnesium and calcium carbonates; certain of them contain also iodides, bromides, and salts of lithium, manganese, and cesium. All contain considerable proportions of dissolved gas, which begins to escape when the water reaches the surface of the earth, and consists largely of carbon dioxide.

T. H. P.

Manganese in Some Springs of the Central Rock System. F. JADIN and A. ASTRUC (*Compt. rend.*, 1914, 159, 332—333. Compare A., 1913, ii, 870; this vol., ii, 378).—The authors have determined the manganese content of the water from seventy-two springs spread over eighteen different places in the central plateau. The waters of this system are, on the whole, richer in manganese than those of the Vosges Mountains, this being expected, as these springs are richer in hydrogen carbonates than those in the Vosges Mountains. As in the previous cases, very marked variations were found in the manganese content of springs at the same place, this variation being relative to the variation in iron content. W. G.

Analytical Chemistry.

Panel for Electro-Analysis. HENRY ZIEGEL (*J. Amer. Chem. Soc.*, 1914, 36, 1450—1452).—A convenient form of supply and switch-board is described; the various connexions allow the use of the current from a 6-volt accumulator or from a 110-volt lighting circuit. W. P. S.

Method for the Preparation of Dry Starch, Soluble in Cold Water, for Use as an Indicator. ROBERT M. CHAPIN (*J. Ind. Eng. Chem.*, 1914, 6, 649—650).—Four hundred grams of potato starch, 2300 c.c. of water, and 80 c.c. of *N*/1-hydrochloric acid are mixed in a flask and heated in a boiling water-bath for 1½ hours. The mixture is then cooled to 50°, rendered ammoniacal, 800 c.c. of 95% alcohol are added, the solution is strained through coarse muslin, and, while still warm (45°), is poured slowly, with continuous stirring, into 4 litres of 95% alcohol. After forty-eight hours the alcohol is decanted, the residue is washed with 95% alcohol, and spread out in a thin layer to dry. The powdered starch thus obtained dissolves readily in cold water. W. P. S.

Apparatus for Controlling the Rate of Flow of Reagents into Solutions, etc. GEORG PANOPULOS (*Chem. Zeit.*, 1914, **38**, 922).—A cover-glass for beakers is provided with a conical hole in its centre; a conical glass rod fits into this hole and extends to the bottom of the beaker. The reagent to be added is poured into the upper or concave side of the cover-glass, and flows slowly into the beaker when the rod is raised slightly. The reagent may also be contained in a graduated vessel fitted over the upper part of the rod, so that a definite amount is admitted to the beaker when the rod is raised.

W. P. S.

A Pipettometer. W. D. FROST (*J. Amer. Chem. Soc.*, 1914, **36**, 1785—1787).—This apparatus consists essentially of a vertical, graduated glass tube, to the upper end of which non-graduated pipettes may be attached by means of rubber tubing. At the lower end of the graduated tube another tube is attached by means of a flexible rubber joint. This tube has a bulb at its outer end, and is so arranged that this end can be readily raised or lowered. The vertical tube and the movable arm with the bulb are partly filled with mercury. The whole apparatus is supported by a suitable frame so arranged on a stand that its height can be varied. By moving the bulb up or down, the height of the mercury in the vertical tube can be altered. When the mercury column is lowered, the pipette draws up the liquid in which its tip is immersed, and when it is raised the liquid is expelled. The quantity of liquid taken up or discharged is measured by reading the position of the mercury in the graduated tube.

The apparatus is very useful for the accurate measurement of small volumes of liquids. It was devised for use in bacteriological work, and is recommended for handling poisonous or infectious material. It can also be employed for calibrating pipettes.

E. G.

Analysis of Very Small Quantities of Gas; Application to the Analysis of Air. PH. A. GUYE and F. E. E. GERMANN (*Compt. rend.*, 1914, **159**, 154—157).—A description of a volumeter by means of which it is possible to analyse very small quantities of gas. The apparatus consists essentially of a volumeter of comparatively small capacity (25–50 c.c.) used in conjunction with a MacLeod vacuum gauge. The measurements are all made at constant volume under a pressure of 7–8 mm., the gauge being sensitive to 1/100 mm. of mercury. The sensitiveness of the apparatus can be considerably augmented by reducing the capacity of the volumeter and increasing the accuracy of the gauge. Absorption and reaction chambers are sealed on to the volumeter, and separated from it by glass taps. The apparatus is figured in the text, and can be used for the analysis of the atmosphere at different heights or of gases evolved on heating solids. Two analyses of the same sample of air, 0.25 c.c. being used in each case, gave exactly the same percentage of oxygen.

W. G.

Gas Analysis by Fractional Distillation at Low Temperatures. G. A. BURRELL and F. M. SEIBERT (*Chem. News*, 1914, 110, 2—5, 14—16; *J. Amer. Chem. Soc.*, 1914, 36, 1537—1548).—A process is described for the separation of a natural gas into its constituent paraffin hydrocarbons by means of fractional distillation of the liquefied gas under low pressures. A measured volume of gas (about $\frac{1}{2}$ litres is sufficient) is transferred to a condensing tube immersed in liquid air in a Dewar flask. This tube is also connected with a Töpler pump fitted with a mercury manometer and with vessels for trapping the gas fractions over mercury as they are removed. The entire sample having been liquefied, the methane can be removed between -185° and -190° at 22 mm. At this temperature ethane has so small a vapour-pressure that none could be detected in the distillate within the limits of analytical error. After thrice-repeated distillation of the residue, no more methane could be removed, and the manometer pressure sank to zero. In a similar way ethane was removed at -140° to -145° . At this temperature, a small quantity of propane also passed over, and was removed by liquefaction and repeated distillation. Propane was separated from the butanes at -120° to -135° by a repetition of the above processes. The final fractions of each gas that were obtained were analytically pure, and the process, although tedious, is therefore applicable for the satisfactory separation of a gaseous mixture into its constituents when this is unattainable by other means. G. F. M.

Penot's Chlorometric Method. J. CLARENS (*Compt. rend.*, 1914, 159, 183—185).—Penot's method of estimating hypochlorites gives results which are lower and less correct than those obtained by Mohr's modification of this method. The following is the simplest and quickest method of carrying out an estimation. A first determination is made by Penot's method of the volume of sodium arsenite solution required. The volume of liquid, thus determined, is poured into a flask, and the solution of the hypochlorite added, the mixture being shaken. A further quantity of sodium arsenite is then added drop by drop until the end of the action is reached, as indicated by starch-iodide paper. The addition of a small amount of potassium bromide to the hypochlorite solution is advantageous in that the end-point can be found without the use of the starch-iodide paper. W. G.

Direct Iodometric Estimation of Soluble Iodides. W. STÜWE (*Chem. Zentr.*, 1914, i, 2121; from *Apoth. Zeit.*, 1914, 29, 382).—The estimation depends on the reaction between iodides and iodates in acid solution, according to the equation $5\text{HI} + \text{HIO}_3 = 6\text{I} + 3\text{H}_2\text{O}$. Ten c.c. of an aqueous solution containing 0.2 gram of potassium iodide are treated with 10 c.c. of 3% potassium iodate solution, 10 c.c. of alcohol and 2 c.c. of nitric acid are added, and 2 grams of barium carbonate mixed with water are then introduced. When the evolution of carbon dioxide has ceased, potassium iodide is added to dissolve the liberated iodine, the

solution is diluted to 100 c.c., and, after settling, 50 c.c. of the clear solution are titrated with *N*/10-thiosulphate solution. The presence of chlorides does not interfere with the estimation, but the method cannot be used when the iodide contains bromide.

W. P. S.

Estimation of Total Sulphur in Caoutchouc. Urz (*Chem. Zentr.*, 1914, i, 2068—2069; from *Gummi-Zeit.*, 1914, 28, 631—632).—A method described recently by Kaye and Sharp (*India Rubber Journal*, 1912), in which the caoutchouc is ignited with a mixture of zinc oxide and potassium nitrate, yields trustworthy results. The crucible containing the mixture should be heated first on an iron plate, and then over a flame which is raised gradually. Experiments with pure sulphur showed that there is no loss under these conditions.

W. P. S.

Estimation of Dissolved Oxygen in Waters, Effluents, etc. PERCY KAYE (*Chem. News*, 1914, 110, 49).—Two methods are described, and depend on the oxidation of ferrous or manganese salts in alkaline solution. A 500 c.c. bottle is filled with the water under examination, 1 gram of ferrous sulphate and 3 grams of potassium hydroxide are added, the closed bottle is shaken occasionally for two hours, the mixture being then acidified with sulphuric acid, and the excess of ferrous sulphate titrated with permanganate solution. In the second method, the water is similarly treated with 1 gram of manganous sulphate, a small quantity of potassium hydroxide, and a few crystals of potassium iodide; after two hours the mixture is acidified with hydrochloric acid, and the liberated iodine is titrated.

W. P. S.

Volumetric Estimation of Sulphurous Acid in Wines. L. FERRÉ (*Bull. Assoc. Chim. Suer. Dist.*, 1914, 31, 959—963).—The wine (100 c.c.), with 2 c.c. of phosphoric acid, is gently boiled for half an hour in a reflux apparatus connected with two Strauss and Wurtz's absorption vessels containing, respectively, solutions of iodine (40 c.c.) and sodium thiosulphate (5 c.c.). Carbon dioxide is passed through the whole apparatus for some minutes before the wine is heated and during the heating. The two solutions are then transferred to a beaker and titrated with thiosulphate solution, with soluble starch as indicator (Mathieu, A., 1910, ii, 747). The iodine solution contains 3.968 grams of iodine per litre, 1 c.c. corresponding with 1 mg. of sulphur dioxide. The thiosulphate solution contains 7.740 grams per litre.

The combined sulphurous acid is estimated, in a similar apparatus, in 100 c.c. of the wine, an amount of iodine solution equivalent to the total sulphurous acid, as previously estimated, and the same amount of a solution of sodium arsenite. The amount of combined sulphur dioxide = $10[40 - (n + 5)]$, *n* being the number of c.c. of iodine solution added to the wine.

The sodium arsenite solution is prepared by dissolving about 1 gram of arsenious acid and 3 grams of crystallised sodium

carbonate in 500–600 c.c. of water. The solution is then made equivalent to the iodine solution.

N. H. J. M.

Apparatus for the Estimation of Hydrogen Sulphide in Water. GEO. B. FRANKFORTER (*J. Ind. Eng. Chem.*, 1914, 6, 676–677).—The apparatus is all in one piece, and consists of a burette and a flask, or bulb, holding 500 c.c.; a three-way tap is provided between the burette and the flask, a side-tube on the neck of the flask being also fitted with a three-way tap. Both these taps are turned so that the flask is in communication with the air; the apparatus is then immersed in the water of which a sample is to be taken, and, on withdrawing the apparatus, a portion of the water flows out of the tap on the side-tube, leaving the flask filled to a definite level. Starch solution is then admitted through the side-tube, and the water is titrated with iodine solution contained in the burette. In a modification of the apparatus the flask is provided with a tap at the bottom, and a tube extends from this tap to a definite height in the flask. A tap or stopper is provided at the top of the burette so that the contents of the flask may be shaken during the titration without loss of solution from the burette.

W. P. S.

Micro-Kjeldahl Estimations. A. V. SAHLSTEDT (*Chem. Zentr.*, 1914, i, 2121; from *Skand. Arch. Physiol.*, 1914, 31, 367–380).—The method proposed by Pilch (A., 1911, ii, 225) was found to be more trustworthy than that described by Folin and Farmer (A., 1912, ii, 702).

W. P. S.

Detection of Nitric Acid with Ferrous Sulphate. I. BELLUCCI (*Ann. Chim. Applicata*, 1914, 1, 549–558).—In presence of ferrous sulphate and sulphuric acid, selenious acid in small proportion undergoes reduction to selenium, which at first forms a purple coloration. This cannot, however, be confused with the coloration given by nitric acid, since the selenium rapidly settles to the bottom of the liquid in a finely divided state.

In the reaction with nitric acid, this is first reduced to nitric oxide, and if the latter acts on aqueous ferrous sulphate, in the presence or absence of a small proportion of sulphuric acid, the dark-brown cation, $\text{Fe}(\text{NO})^{++}$, is formed; here the iron remains bivalent, and the nitric oxide functions as a neutral molecule. When the solution contains sulphuric acid, the salt $\text{Fe}(\text{NO})\text{SO}_4$ is formed. The complex cation is readily dissociated, and the nitric oxide may be completely eliminated from the solution and the coloration destroyed by heating. In testing for nitric acid, it is therefore necessary to prevent excessive rise of temperature of the liquid.

When, however, nitric oxide acts on a solution of ferrous sulphate containing sulphuric acid in sufficient concentration, the liquid assumes an intense amethyst-red coloration, which changes to brown on slight dilution with water, the reverse change being subsequently effected by addition of concentrated sulphuric acid.

Under the influence of an electric current, the coloured zone of the red solution migrates towards the anode, whilst that of the brown liquid moves to the anode. In the case of the red solution, the colour is due to the anion, $\text{Fe}(\text{SO}_4)_2\text{NO}$.

If the nitric acid is mixed with the ferrous sulphate and sulphuric acid, there is a risk of the immediate oxidation of the ferrous iron by the acid and of the prevention of the formation of the cation $\text{Fe}(\text{NO})$. When, however, the liquids are in layers, the nitric acid is in excess only at the zone of contact, so that time is allowed for the manifestation of the coloration (see below); a further advantage of this procedure is the possibility of using concentrated sulphuric acid and an excess of ferrous sulphate together, the limited solubility of the salt in the acid otherwise coming into play.

The reduction of the nitric acid by the ferrous sulphate takes place rapidly in presence of concentrated sulphuric acid, and only slowly, or not at all, if the proportion of sulphuric acid present is small. The volume of acid taken should be at least as great as that of the liquid to be tested, and the nitrate should either be dissolved in a little water or, when this is not possible, be added in the solid state to the sulphuric acid.

The best results are obtained by mixing the nitrate solution with the sulphuric acid, and by pouring the cold, saturated ferrous sulphate solution carefully on to the surface of the mixture while the latter is still hot. Equal rapidity of action is obtained by introducing a mixture of the ferrous sulphate and the nitrate solutions on to the surface of the sulphuric acid, but the intensity of the coloration and the thickness of the ring are less than in the former case, whilst the coloration disappears more rapidly. When the nitrate solution forms the upper layer, and the mixture of ferrous sulphate and sulphuric acid the lower one, the test is considerably less delicate.

When attention is paid to the above points, 1 part of nitric acid can be detected in 250,000 parts of sulphuric acid. If, however, small traces of nitric acid are to be sought, the use of strata loses its objects, and the best results are obtained by mixing the solutions. For this end, 2.5 grams of ferrous sulphate are dissolved in 6–8 c.c. of water containing a few drops of dilute sulphuric acid, and the solution added to 1000 grams of 90% sulphuric acid (compare Manchot and Huttner, A., 1910, ii, 414). This reagent remains unchanged for a long time in a closed vessel, and allows of the detection of 1 part of nitric acid in 500,000 of sulphuric acid.

T. H. P.

Fresenius' Method for Estimating Small Quantities of Nitrites and its Sensitiveness Compared with the *m*-Phenylenediamine Reaction. E. A. LETTS and FLORENCE W. REA (*Analyst*, 1914, 39, 350–352).—The zinc iodide-starch solution described by Fresenius for the colorimetric estimation of nitrites was found to be capable of detecting as little as 0.00025 mg. of nitrite-nitrogen, and to be about twenty times more sensitive than

the *m*-phenylenediamine reaction. A freshly prepared zinc iodide-starch reagent appears to be less sensitive than a similar solution one year old.

W. P. S.

Use of Ammonium Citrate in the Estimation of Phosphoric Acid [in Slags]. A. QUARTAROLI and A. ROGAI (*Chem. Zentr.*, 1914, ii, 263—264; from *Staz. sperim. agrar. ital.*, 1914, 47, 410—426).—The chief sources of error in the estimation of phosphoric acid in Thomas slag lie in the precipitation of magnesium iron compounds and in the incomplete precipitation of the phosphoric acid with magnesia mixture. When the magnesium pyrophosphate is not quite white, the presence of iron is indicated; this may be removed by treatment with “cupferron.” The citrate method cannot be used when iron and aluminium phosphates are present.

W. P. S.

Estimation of Arsenic in Organic Substances. MARIAM VINOGRAD (*J. Amer. Chem. Soc.*, 1914, 36, 1548—1551).—For the oxidation of organic matter previous to the estimation of arsenic in such substances as blood, tissue, etc., it is recommended that the substance be heated with nitric acid at 260° in a sealed tube. One c.c. of nitric acid is sufficient to oxidise 3 c.c. of blood serum, the residue obtained on evaporating 100 c.c. of spinal fluid, or 0.5 gram of dry tissue. After the oxidation, the contents of the tube are diluted, evaporated to a small volume, and heated with sulphuric acid until all nitric acid has been expelled. The arsenic is then estimated by Sanger and Black's modification of the Gutzeit method (*A.*, 1908, ii, 64).

W. P. S.

Estimation of Potassium and Magnesium by Physico-chemical Volumetric Methods. Application to the Analysis of Wines. MARCEL DUBOUX (*Compt. rend.*, 1914, 159, 320—323. Compare Dutoit and Duboux, *A.*, 1908, ii, 781, 892).—Potassium can be estimated in wines by determining the conductivity of the solution after the repeated additions of small amounts of chloroplatinic acid, after the addition of eighteen times its volume of alcohol. A change in the direction of the conductivity curve indicates the end of the precipitation. It is necessary to wait some time for the conductivity to become constant after each addition of the reagent, and also to destroy the organic matter in the wine by evaporation and ignition prior to the estimation. For the estimation of magnesium, the conductivity is measured in a solution containing 0.02% of ammonia and 0.06% of ammonium chloride after the addition of measured small quantities of *N*/2-phosphoric acid. Before performing the titration, the organic acids in the wine must be destroyed and the phosphoric acid and lime removed by precipitation. Fifty c.c. of the wine are treated with 3 c.c. of *N*-sulphuric acid and 100 c.c. of alcohol. After two hours the calcium sulphate is filtered off, and to the filtrate is added 3.5 c.c. of *N*-ammonia and 7 c.c. of a 16% solution of lead nitrate, which precipitates the phosphates. The whole is warmed on the water-

bath, filtered, and to the filtrate 5 c.c. of *N*-sulphuric acid are added and the lead sulphate filtered off. The solution is evaporated to dryness and calcined, the residue is dissolved in 5 c.c. of *N*/10-HCl, 50 c.c. of *N*/10-ammonia are added, and the liquid titrated with the phosphoric acid.

W. G.

Estimation of Calcium in Urine and Faeces. R. VON DER HEIDE (*Biochem. Zeitsch.*, 1914, 65, 363—380).—A detailed investigation is made of the estimation of calcium by Aron's method, according to which the metal is precipitated as sulphate by alcohol in the liquid obtained after the destruction of organic matter by Neumann's wet-ashing method. It is shown that this method of precipitation of calcium has many sources of error, due to the fact, chiefly, that other substances are carried down with the calcium sulphate precipitate. The author recommends the following modification. The calcium sulphate precipitate is collected on a Gooch filter, and then dissolved in hot concentrated hydrochloric acid. The solution is neutralised to methyl-orange with ammonia, and ferric chloride (two to three drops of 10% solution) and acetate are added. In the hot filtrate from the precipitate thus produced, the calcium is precipitated as oxalate.

S. B. S.

Estimation of Magnesia in Magnesite. HENRYK WDOVISZEWSKI (*Chem. Zeit.*, 1914, 38, 949—950).—In the estimation of magnesia by Mayrhofer's method (A., 1908, ii, 431), it is essential that the mixture be kept at 0° for two hours after the ammonium magnesium phosphate has been precipitated. The precipitate is then collected, washed with ammonia, dissolved in hydrochloric acid, reprecipitated by the addition of ammonia, and again cooled for two hours before being finally collected, dried, ignited, and weighed.

W. P. S.

Estimation of Copper as Cuprous Sulphide. ERNST MURMANN (*Chem. Zentr.*, 1914, i, 2016; from *Oesterr. Chem. Zeit.*, 1914, [ii], 17, 96).—A reply to C. Beck (A., 1913, ii, 1077), maintaining that the conversion of cupric into cuprous sulphide by ignition in a current of carbon dioxide should be rejected.

N. H. J. M.

Estimation of Copper in Open Hearth and Alloy Steel or in Cast Iron. E. D. KOEPPING (*J. Ind. Eng. Chem.*, 1914, 6, 696).—From 3 to 10 grams of the steel are dissolved in 35 c.c. of hydrochloric acid (1:1), the solution is diluted with 35 c.c. of water, and boiled for twenty minutes after the introduction of a strip of sheet aluminium. The solution is then filtered, the precipitated copper is washed with hot water, and dissolved in a mixture of 3 c.c. of nitric acid and 7 c.c. of water; this acid solution is first poured over the strip of aluminium to dissolve adhering copper. The solution and washings are boiled for fifteen minutes to expel nitrous fumes, 7 c.c. of ammonia are added, and the boiling continued until only a small quantity of free ammonia remains.

Ten c.c. of 80% acetic acid are now added, the mixture is boiled for one minute, cooled, potassium iodide is added, and the liberated iodine titrated with thiosulphate solution.

W. P. S.

Estimation of Iron by Permanganate in the Presence of Hydrochloric Acid. O. L. BARNEBY (*J. Amer. Chem. Soc.*, 1914, **36**, 1429-1448).—Sodium sulphate, acid phosphate mixtures, manganese sulphate with sulphuric acid or phosphoric acid, and cerous sulphate, may be employed in the titration of a hydrochloric acid solution of ferrous salts in order to prevent the action of the hydrochloric acid on the permanganate used for the titration.

W. P. S.

Estimation of Iron in the Presence of Phosphoric Acid. C. E. CORFIELD and W. R. PRATT (*Pharm. J.*, 1914, **93**, 131-133).—The gravimetric estimation of iron in the presence of even small quantities of phosphate is untrustworthy, the results obtained being too high and not concordant. Volumetric methods are preferable; the iodometric process and reduction by stannous chloride may be employed in the presence of phosphoric acid, but the former process is liable to give slightly high results, owing to oxidation of the hydriodic acid on contact with air. Reduction of ferric salts by zinc or zinc-couples has the disadvantage that the subsequent titration with dichromate solution cannot be carried to completion.

W. P. S.

Estimation of Chromium and Manganese in Iron and Steel. FRED C. T. DANIELS (*J. Ind. Eng. Chem.*, 1914, **6**, 658-659).—The metals are estimated by the persulphate method. Chromium is estimated by dissolving 1 gram of the sample in 100 c.c. of nitric acid (D 1.135), boiling the solution to expel nitrous fumes, and then adding 75 c.c. of a 0.2% silver nitrate solution and 5 grams of ammonium persulphate. The mixture is boiled for one minute, and hydrochloric acid is added drop by drop until the permanganate has been reduced. The boiling is continued for one minute, the solution is then cooled, an excess of $N/10$ -ferrous ammonium sulphate is added, and the mixture titrated with $N/10$ -permanganate solution. The number of c.c. of $N/10$ -ferrous ammonium sulphate solution oxidised by the chromate is multiplied by 0.00174 to obtain the quantity of chromium in the sample. Chromium and manganese are then estimated together in a separate portion of the sample. The same procedure is adopted, except that, after the addition of the persulphate, the solution is heated just to boiling, then cooled immediately, and treated with an excess of ferrous ammonium sulphate solution.

W. P. S.

Volumetric Estimation of Titanium and Chromium by means of a Modified Reductor. C. VAN BRUNT (*J. Amer. Chem. Soc.*, 1914, **36**, 1426-1429).—The reductor described is of the type proposed by Shimer and Shimer (*A.*, 1913, ii, 723), but has a height

of about 20 cm., and is heated electrically by passing a current through a length of resistance ribbon wrapped round the exterior of the tube. For the analysis of a mixture containing iron, chromium, and titanium, the metals are brought into solution as their sulphates; a portion of the solution is treated with bismuth oxide, passed through the reductor, and the reduced solution is titrated; this gives the quantity of iron. A second portion is then reduced and titrated, the result giving the quantity of the three metals together. Chromium is estimated in another portion of the solution, by titration with a ferrous salt solution, after it has been converted into chromate by heating with ammonium persulphate.

W. P. S.

Anomalies in the Analysis of Platinum Minerals. H. C. HOLTZ (*Ann. Chim.*, 1914, [ix], 2, 56—63. Compare this vol., ii, 144).—Polemical. A reply to Wunder and Thüringer (*A.*, 1913, ii, 883).

W. G.

Estimation of Iridium in Platinum-Iridium Alloys. C. O. BANNISTER and E. A. DU VERGIER (*Analyst*, 1914, 39, 340—346).—Two methods are given; in the first, the platinum-iridium is alloyed with silver and parted, whilst in the second it is alloyed with lead and parted. *Method 1*: A quantity of 0.25 gram of the alloy is cupelled with 1.5 grams of pure silver and 10 grams of assay lead; when the last traces of lead have disappeared, the button is parted twice with 40 c.c. of concentrated sulphuric acid, and the insoluble residue washed with water, annealed at a high temperature, then digested with *aqua regia*, diluted with water, and the insoluble residue of iridium collected on a filter. After being washed with ammonia to remove traces of silver chloride, the iridium is ignited at a high temperature and weighed. If desired, the platinum may be estimated in the *aqua regia* solution. *Method 2*: 0.5 Gram of the alloy is melted in a carbon crucible with 5 grams of lead, the lead button is repeatedly digested with hot dilute nitric acid, and the insoluble residue then treated with *aqua regia* as described in method 1. Both methods yield trustworthy results.

W. P. S.

Estimation of Organic Matter in Water. PERCY KAY (*Chem. News*, 1914, 110, 13).—Potassium ferricyanide is recommended as an oxidising agent in preference to the method of Tidy usually employed, where the oxygen absorbed is much below the quantity actually needed to oxidise the organic matter. The procedure is as follows: About 500 c.c. of the water with 1.1 gram of ferricyanide and 3.5 c.c. of concentrated potassium hydroxide solution are boiled for an hour, and, after cooling, the excess of ferricyanide is determined by the addition, after acidification, of potassium iodide and excess of zinc sulphate, and titration of the liberated iodine with thiosulphate in slightly alkaline solution. The difference between the observed reading and a blank experiment is a measure of the oxygen absorbed by the organic matter.

A water giving an oxygen absorption of 2.56 per million by this process gave 2.34 by Wanklyn's moist combustion method, and only 0.72 by the ordinary method. G. F. M.

Detection of Methyl Alcohol. A. RINCK (*Zeitsch. Nahr. Genussm.*, 1914, 28, 98—99).—A small quantity of the alcoholic solution to be tested is distilled slowly, and the vapours are passed through a silica tube containing a copper spiral, which is maintained at a red heat by a flame placed below the tube. The distillate is collected in a cooled receiver, and a portion of it is tested with sulphuric acid and morphine for the presence of formaldehyde. W. P. S.

Application of Physico-chemical Methods in the Analysis of Wines. G. LO PRIORE (*Ann. Chim. Applicata*, 1914, 1, 494—502).—The author discusses, and gives a bibliography of, the physico-chemical methods used in estimating the alcohol and acidity of wines, and in determining the distribution of the bases among the acids. T. H. P.

Capillary Method of Estimating the Acidity of Wines. R. DUBRISAY and X. ROCQUES (*Ann. Falsif.*, 1914, 7, 341—346).—The method described previously by one of the authors (A., 1913, ii, 388) yields satisfactory results when applied to certain wines, but its usefulness is limited. It may be employed as a control method in comparing the acidity of two samples of wine. W. P. S.

Estimation of Organic Phosphorus Compounds in Concentrated Musts and Wines. CESARE FINZI (*Chem. Zentr.*, 1914, ii, 88; from *Staz. sperim. agrar. ital.*, 1914, 47, 337—346).—One hundred c.c. of the must are evaporated at 47° under reduced pressure to a syrup; this is mixed with sand, dried over sulphuric acid under reduced pressure, and then extracted in a Soxhlet apparatus for twelve hours with anhydrous ether. The extraction is then continued for twelve hours with absolute alcohol, the pressure being reduced so that the temperature does not exceed 48°. The alcoholic extract is evaporated under reduced pressure, the residue fused with a mixture of potassium nitrate and sodium carbonate, and the resulting phosphate estimated by the molybdate method. In the case of wine, 500 c.c. of the sample are evaporated to dryness under reduced pressure, the residue extracted five times with anhydrous ether, then five times with absolute alcohol at 45°, and the alcoholic extract is treated as described. When the molybdate precipitate is converted into ammonium magnesium phosphate and weighed as magnesium pyrophosphate, the weight of the latter multiplied by 7.2703 gives the quantity of lecithin present. The organic phosphorus compounds appear to be derived from the juice and fleshy portions of the fruit, and, whilst there is no definite relation between the quantities of organic and inorganic phosphorus, a certain relation exists between the organic phosphorus and the protein-content. W. P. S.

Estimation of Glycerol in Industrial Glycerins and in Soap Lyes. M. TORTELLI and A. CECCHERELLI (*Ann. Chim. Applicata*, 1914, 1, 514—548).—The authors have investigated the "acetin" method recommended for the estimation of glycerol in crude glycerins by the International Committee in their publication of January, 1911. They find: (1) that this method is subject to a fundamental error, and must yield somewhat inaccurate results; (2) that Hefner's dichromate method, when slightly modified, gives exact results. Full details of this modified process, in its application to crude glycerins and to soap lyes, are given, together with the necessary tables. T. H. P.

The Estimation of Esters in Essential Oils. JEAN NIVIÈRE (*Bull. Soc. chim.*, 1914, [iv], 15, 677—680).—The author considers that the standard method for estimating esters in essential oils, using a long glass condenser, is accurate and gives concordant results, and that Béhal's modification, using a closed tube at 100° (compare this vol., ii, 686), is unnecessary. Further, the high results obtained in the case of oils of lavender and of bergamot when using a closed tube are not due to linalool. W. G.

Cupropotassic Solutions, Barreswill's and Fehling's Solutions. H. PELLET (*Bull. Assoc. Chim. Sucr. Dist.*, 1914, 31, 978—981).—More than fifty cupropotassic solutions are known. They may be divided into four groups, in which (1) potassium hydrogen tartrate, (2) potassium sodium tartrate, (3) potassium tartrate, and (4) tartaric acid are employed. As the original process for estimating sugar in this manner was published by Barreswill (in 1843), and was, for several years, known as Barreswill's method, it is suggested, in accordance with the proposal recently made by Lindet, that the name "Barreswill solution" should be employed instead of "Fehling solution." N. H. J. M.

Different Methods of Inversion. A. GILLET (*Bull. Assoc. Chim. Sucr. Dist.*, 1914, 31, 992—1033).—A study of the methods of Clerget, Herzfeld, Andriik, Pellet, Saillard, and Ogilvie. As regards direct acid polarisation, both Pellet's and Andriik's methods may be employed for molasses. Pellet's method is, however, preferred, and it is applicable to all sugar products.

Methods in which direct alkaline polarisation is compared with indirect acid polarisation should not be employed.

As regards beet juice, the different methods of inversion give less regular results than in the case of molasses. Pellet's and Andriik's methods seem, however, to give the same results.

N. H. J. M.

Polarimetric Estimation of Lactose in Milk. E. FEDER (*Zeitsch. Nahr. Genussm.*, 1914, 28, 20—29).—The use of mercuric iodide and sulphuric acid, as in Scheibe's method, for precipitating casein and fat from milk previous to the estimation of lactose cannot be recommended, owing to the difficulty of ascertaining the

volume of the resulting precipitate; moreover, the rotatory power of the lactose is considerably influenced by the mercuric iodide and sulphuric acid mixture. When, however, the milk is curdled by the addition of asapol, the precipitate consists essentially of proteins and fat, and its volume is approximately equal to the quantity of the total solids of the milk, less lactose and mineral matter. The following process is described for the estimation: Seventy-five c.c. of the milk are treated in a 100 c.c. flask with 6 c.c. of a reagent prepared by dissolving 75 grams of asapol and 75 grams of citric acid in hot water, and diluting the solution to 250 c.c. The treated milk is then diluted to 100 c.c., shaken, filtered after fifteen minutes, and the filtrate polarised at 20° in a 200 mm. tube; under these conditions, each degree of rotation observed is equivalent to 0.9518 gram of lactose. The reading found is multiplied by 0.9518; let the result be a , then the actual quantity of lactose, L , is calculated from the equation

$$L = a\{100.8 - t + (96.7 - f)a/75\}/75,$$

where t is the percentage of total solids and f the percentage of fat in the milk.

W. P. S.

Estimation of Dextrin and Sugars in Foods. C. F. MUTTELET (*Ann. Patisf.*, 1914, 7, 372—380).—In a solution, containing from 5 to 10 grams (total) per 100 c.c., of sucrose, dextrose, lævulose, and dextrin, the following estimations are made: (1) The reducing power of the solution is estimated, and the result expressed as grams of invert sugar per 100 c.c., p . (2) The reducing power is estimated after inversion, and the result expressed in the same terms, q . (3) The reducing power is estimated after inversion in an autoclave at 110°, the result being also calculated into grams of invert sugar per 100 c.c., m . (4) The rotation of the solution is determined at 20° in a 200 mm. tube; let D be the reading observed. Then the quantity of sucrose, S , present per 100 c.c. is $0.95(q - p)$, having a rotation, c , equal to $1.33 \times S$. The amount of dextrin, Δ , is $0.90(m - q)$, having a rotation, δ , of $3.90 \times \Delta$. The sum of the weights of the dextrose, G , and the lævulose, L , is equal to p , and the corresponding rotation, d , is $D - (c + \delta)$. The quantity of lævulose is, therefore, $(1.06 \times p) - d$ grams, and of dextrose, $(p - L)$ grams.

W. P. S.

Criterion for the Genuineness of Vinegar. N. TARUGI (*Boll. Chim. Farm.*, 1914, 53, 129—137).—After its acidity has been determined, the vinegar is diluted so as to contain 0.6% of acetic acid ($V = 10,000$), and its electrical conductivity measured at 25°. Examination of a series of thirty-three samples of genuine vinegar gave 7.92, 9.81, and 11.36 as the minimal, mean, and maximal values of the molecular conductivity, M . Under similar conditions, the value for pure acetic acid was found to be 5.69, and that for a commercial sample containing 31.8% of acid 5.70; the molecular conductivity of vinegar would therefore be appreciably lowered by the addition of any considerable proportion of acetic acid. Commercial samples which had been adulterated with from

0.5% to 3.8% of sodium chloride, or with 2.0% of potassium sulphate, gave molecular conductivities varying from 11.81 to 18.88. The addition of small proportions of mineral acids also increases the conductivity. Thus, for diluted vinegars containing 0.59% of acetic acid and 0.01% of hydrochloric, sulphuric, and nitric acid respectively, the values of the molecular conductivity were 14.99, 14.20, and 12.27, the value for the original vinegar being 11.10.

The vinegar was next neutralised with sodium hydroxide prepared from the metal, diluted to $V=10,000$, and the conductivity again measured at 25°. After this treatment, a series of nineteen samples of genuine vinegar gave values for the molecular conductivity, M' , varying between 59.4 and 88.05. The ratio $M':M$ has the minimal, mean, and maximal values 6.66, 7.94, and 9.98 respectively. The corresponding value for pure acetic acid is 12.14, whilst the vinegars adulterated with sodium chloride or potassium sulphate gave values between 4.17 and 5.72, and those containing 0.01% of hydrochloric, sulphuric, and nitric acids the values 4.82, 4.77, and 5.67 respectively. A sample of vinegar which was suspected to contain added acetic acid gave $M=7.65$, $M'=82.1$, and $M':M=10.7$.

No relation exists between the value of the ratio $M':M$ and the proportion of dry extract present in a vinegar. T. H. P.

Estimation of Ricinoleic Acid in Oil Preparations. FRANZ ERBAN (*Chem. Zentr.*, 1912, ii, 358; from *Seifenfabrikant*, 1914, 34, 493—495, 525—527, 556—557, 585—587).—Owing to the tendency of ricinoleic acid to form polymerides, the acid number does not indicate the quantity of this acid in fatty acid mixtures; for instance, whilst the acid number of ricinoleic acid is 188, that of di-ricinoleic acid is 96.8. The polymeric acids are, however, converted into the normal acid when submitted to saponification, and the acid number of the fatty acids obtained from the soap gives the proportion of ricinoleic acid present provided that the alteration in weight of the fatty acid mixture is taken into account. Formulæ are given in the original paper for calculating the composition of a mixture of ricinoleic acid and diricinoleic acid, of ricinoleic acid, diricinoleic acid, and neutral fat, of ricinoleic acid, lactide, and diglyceride, etc. W. P. S.

Estimation of Lactic Acid in Wine by Moslinger's Barium Chloride Method. W. I. BARAGIOLA and O. SCHUPPLI (*Zeitsch. Nahr. Genussm.*, 1914, 27, 841—881).—The following modification of the method is proposed, since the process as described originally (A., 1902, ii, 180) is liable to give untrustworthy results, owing to the reduction of barium chloride by carbon, to the retention of lactic acid by the alcohol-insoluble substances, and to the conversion of a portion of the lactic acid by malic acid into a compound in which the former acid is not estimated. Twenty-five c.c. of the wine are mixed with 25 c.c. of water, and distilled with steam until 200 c.c. of distillate have been collected; this distillate is treated with 5 c.c. of 10% barium chloride solution, and neutralised with

saturated barium hydroxide solution. In case any lactic anhydride is present, an excess of barium hydroxide may be added, the solution heated for ten minutes on a water-bath, and then neutralised with hydrochloric acid, using azolitmin paper as the indicator. The neutral solution is evaporated to 15 c.c., transferred to a 100 c.c. cylinder, diluted with water to 25 c.c., and 95% alcohol is added drop by drop while the mixture is shaken. The mixture is now diluted to 100 c.c. with alcohol, filtered after twenty-four hours, and 75 c.c. of the filtrate are treated with 25 c.c. of 5% sodium sulphate solution. The barium sulphate is removed by filtration, and 75 c.c. of the filtrate are evaporated to dryness; the residue is incinerated, the ash dissolved in water, and the boiling solution titrated with *N*/10-acid.

W. P. S.

Colour Reaction of Citric Acid. E. P. HÄUSSLER (*Chem. Zeit.*, 1914, 38, 937).—The solution to be tested is mixed with a few c.c. of an alcoholic vanillin solution and evaporated to dryness; the residue is then heated on a water-bath for fifteen minutes with four drops of dilute sulphuric acid, diluted with water, and rendered ammoniacal. A bright, red coloration is obtained if as little as 0.002 gram of citric acid is present. Tartaric, malic, oxalic, malonic, benzoic, salicylic, acetic, lactic, or succinic acids do not yield the reaction, and their presence does not greatly affect that given by citric acid. The test may be applied to fruit juices after the organic acids have been precipitated with lead acetate and separated as their calcium salts.

W. P. S.

Estimation of Refractivity and Dispersion in Fats and Oils. K. SZALÁGYI (*Biochem. Zeitsch.*, 1914, 66, 149—153).—These factors were determined in the cases of thirty-eight fats and oils at 45°. For the measurement of the dispersion, the light of a hydrogen spectrum was employed. It was found that these factors were not constant for any given oil, depending on the composition, method of preparation, and age of the various samples.

S. B. S.

Examination of Various Methods for the Estimation of the Iodine Number of Fats. St. WEISER and H. G. DONÁTH (*Zeitsch. Nahr. Genussm.*, 1914, 28, 65—73).—Winkler's potassium bromate method is recommended for the estimation of the iodine number of fats, oils, and fatty acids. A weighed quantity of the fat is dissolved in 10 c.c. of carbon tetrachloride, and 50 c.c. of *N*/10-potassium bromate solution, 1.5 grams of potassium bromide, and 10 c.c. of 10% hydrochloric acid are added. After one to four hours (ordinary fats require from one to two hours' contact, fish oils four hours), potassium iodide solution is added, and the liberated iodine is titrated. The results agree with those found by the Hübl, Wys, and Waller methods (compare A., 1910, ii, 1122).

W. P. S.

Preservation of Milk Samples for Analysis. J. TILLMANS, A. SPITTOEBBER, and H. RIFFART (*Zeitsch. Nahr. Genussm.*, 1914, 27, 893—901).—Mercuric chloride was found to be the most suitable

substance for preserving milk samples for subsequent analysis. The addition of 0.04% of mercuric chloride keeps the milk quite fresh for 120 hours, has no influence on the usual methods used in milk analysis, and does not interfere with the detection of nitrates in milk. Various objections are adduced against the use of thymol, phenol, chloroform, mustard oil, sodium fluoride, and potassium dichromate for the purpose mentioned. W. P. S.

Detection of Acetone in Urine by Sobel's Method. BEUTNER (*Chem. Zentr.*, 1914, i, 2207; from *Schweiz. Apoth. Zeit.*, 1914, 52, 293—294).—Sobel's method (this vol., ii, 592) is untrustworthy; in the presence of nitric acid, a portion of the silver iodide, resulting from the decomposition of the iodoform with nitric acid, is converted into silver iodate, which is fairly soluble in dilute nitric acid. Iodine is also lost when the silver iodide containing iodate is ignited. The factor for converting silver iodide into acetone should be 0.082, and not 0.1171 as given by Sobel. W. P. S.

Microchemistry of Some Anthraquinones. EMAN. SENFT (*Chem. Zentr.*, 1914, ii, 82—83; from *Zeitsch. Allg. Osterr. Apoth.-Ver.*, 1914, 52, 165—166, 181—183, 201—202).—Rhodocladonic acid dissolves in sodium carbonate solution, yielding a reddish-brown colour, and the solution reduces potassium permanganate in the cold, with the formation of a red precipitate; the latter is only slightly soluble in the usual solvents, but nitric acid dissolves it to a colourless solution, whilst with sulphuric acid it gives a purple-red coloration. This coloration changes quickly to yellow, and the solution deposits red crystals. The author has detected the presence of rhodocladonic acid in members of the *Gladonia* species by means of these reactions. When heated considerably above its melting point, solorinic acid gives off yellow vapours, and yields a dichroic (greenish-yellow and red), crystalline sublimate, which dissolves in sulphuric acid to a violet solution; this colour changes to yellow, and an amorphous, yellow precipitate is formed; the precipitate crystallises gradually. The crystals thus obtained are coloured first red and then violet when treated with cold 10% potassium hydroxide solution, but are not dissolved; on heating, the alkali converts the crystals into an amorphous, violet precipitate. Solorinic acid is only slightly soluble in hot petroleum. Rhodophyscin, contained in the lichen, *Physcia endococcinea*, separates from boiling acetic acid in the form of orange-red crystals; it does not yield a sublimate. With sulphuric acid it yields a purple-red solution, from which a brown precipitate separates. Potassium hydroxide solution dissolves the substance, yielding a red solution, which afterwards deposits an amorphous, violet precipitate. Rhodophyscin is insoluble in hot petroleum. Blastenin, contained in *Blastenia arenaria* and *B. percrocata*, is soluble in chloroform, and yields a yellow sublimate, which is coloured red, but not dissolved, by potassium hydroxide solution. The sublimate gives a red solution with sulphuric acid; the solution changes to yellow, and lemon-yellow crystals are deposited.

Blastenin dissolves in hot petroleum, and the solution yields orange-yellow crystals. W. P. S.

Detection of Small Quantities of Phloridzin Alone and in the Presence of Phlorin. ERNST GRIESE (*Chem. Zentr.*, 1914, ii, 88—89; from *Beitr. Physiol.*, 1914, 1, 23, 52).—Traces of phloridzin may be detected by means of reactions with ferric chloride, Millon's reagent (brownish-red precipitate), or mercurous nitrate (white precipitate). With ferric chloride and Millon's reagent a reaction is obtained with 1 c.c. of a 0.002% phloridzin test solution; the mercurous nitrate is about five times more sensitive. Phlorin free from phloridzin may be obtained by taking advantage of the slight solubility of the latter in ether and amyl alcohol (compare A., 1912, i, 885). W. P. S.

Estimation of Acetanilide. A. MIRKIN (*Amer. J. Pharm.*, 1914, 86, 354—355).—The method proposed depends on the conversion of the acetanilide into aniline, and the titration of the latter with sodium nitrite solution. One gram of acetanilide is boiled for four hours with a mixture of one part of sulphuric acid (D 1.84) and five parts of water. The solution is then cooled, neutralised with sodium hydrogen carbonate, hydrochloric acid is added (6 mols. to 1 mol. aniline), the mixture cooled to -10° , and titrated with standardised sodium nitrite solution. Potassium iodide-starch paper is used as the indicator; the diazotising reaction proceeds slowly, and several minutes should elapse after the addition of each quantity of the nitrite solution before a drop of the solution is placed on the test paper. W. P. S.

Estimation of Acetanilide and Phenacetin in Admixture. W. O. EMERY (*J. Ind. Eng. Chem.*, 1914, 6, 665—669).—The process described depends on the formation of an insoluble iodine additive compound, or periodide, when phenacetin in aqueous solution is added to an iodine solution containing hydrochloric acid; in the case of acetanilide, the iodine compound is soluble. A quantity of 0.2 gram of the phenacetin-acetanilide mixture is dissolved by warming with 2 c.c. of acetic acid and 40 c.c. of water, and the solution is rinsed into 25 c.c. of $N/5$ -iodine solution, previously heated to 40° ; 3 c.c. of concentrated hydrochloric acid are then added, and, when a crystalline precipitate has formed, the mixture is cooled and diluted with water to about 98 c.c. After eighteen hours the solution is diluted to 100 c.c., filtered, and 50 c.c. of the filtrate are titrated with $N/10$ -thiosulphate solution. Each c.c. of $N/10$ -iodine solution which has entered into combination corresponds with 0.00889 gram of phenacetin. The phenacetin may also be estimated gravimetrically by collecting the precipitate, washing it with iodine solution, then with a small quantity of water, transferring it to a separating funnel, and, after the addition of sodium sulphite, extracting the phenacetin with chloroform. The acetanilide is estimated by treating 30 c.c. of the filtrate from the iodine compound with sodium sulphite and

an excess of sodium hydrogen carbonate, shaking the solution with chloroform, and heating the chloroform solution for one hour on a water-bath with 10 c.c. of dilute sulphuric acid. Ten c.c. of concentrated hydrochloric acid are then added, and the mixture is titrated with standardised potassium bromide-bromate solution.

W. P. S.

New Method for the Estimation of Phenolphthalein. A. MIRKIN (*Amer. J. Pharm.*, 1914, 86, 307—308).—The method depends on the formation of an oxime when phenolphthalein is treated with hydroxylamine. One gram of phenolphthalein, 0.8 gram of hydroxylamine hydrochloride, and 0.52 gram of sodium hydroxide are dissolved in 40 c.c. of absolute alcohol, and the solution is boiled for about three hours under a reflux apparatus until the liquid turns yellow. Water is then added, 10 c.c. of 10% sulphuric acid are introduced, and the solution is diluted to 250 c.c. In 50 c.c. of this solution the acid is neutralised, using methyl-orange as indicator, and the excess of hydroxylamine then titrated with $N/10$ -potassium hydroxide solution, phenolphthalein being the indicator in this case. A blank experiment, using the same quantities of sodium hydroxide, hydroxylamine, and alcohol, is run at the same time, and the difference between the number of c.c. of $N/10$ -alkali solution required in the two titrations is multiplied by 316 to give the quantity of phenolphthalein. For the estimation of phenolphthalein in medicinal tablets, the latter are crushed, extracted with alcohol, and a portion of the alcoholic solution used for the estimation. These tablets frequently contain lactose and sucrose; the latter does not yield an oxime, and lactose is practically insoluble in alcohol.

W. P. S.

A Method of Estimating Urea. A. DESGREZ and R. MOOG (*Compt. rend.*, 1914, 159, 250—253. Compare A., 1912, ii, 104).—A description of a modified form of ureometer (*loc. cit.*), by means of which it is possible to make a rapid and accurate estimation of the amount of urea in urine or serum, 1 c.c. of urine being used. The apparatus is figured in the text, and only requires the use of a small amount of chloroform as compared with the earlier pattern (*loc. cit.*). The reagent used is prepared by dissolving 1 gram of mercury in 2 grams of nitric acid (D 1.3322), and diluting this with an equal volume of a liquid prepared by shaking 1 gram of infusorial earth with 100 c.c. of water, leaving one minute, and then decanting. This suspension acts as a catalyst, and renders the decomposition of the urea complete at 17°. The only other nitrogenous constituent of urine decomposed under these conditions is allantoin, and this only at the rate of 0.015 gram in twenty-four hours. The actual estimation takes about forty-five minutes.

W. G.

Gravimetric Estimation of Small Quantities of Urea at Dilutions Greater than 1 in 1000. R. FOSSE (*Compt. rend.*, 1914, 159, 253—256. Compare this vol., i, 859; ii, 596).—In

order to estimate the amount of urea in solutions containing 1 gram or less of urea in 1 litre, the following process should be adopted. The solution of urea (1 c.c.), exactly measured, is diluted with twice its volume of glacial acetic acid, and then to it is added one-twentieth of its volume of a solution of xanthhydrol in methyl alcohol, this addition being repeated twice at intervals of ten minutes. After one hour, the precipitate is collected in the usual way. An alternative process is as follows. To a mixture containing one volume of the urea solution and two volumes of glacial acetic acid, one-twentieth of its total volume of xanthhydrol solution is added, the whole allowed to remain one hour, and the precipitate collected.

W. G.

Estimation of Small Quantities of Urea by Sodium Hypobromite. W. MESTREZAT (*J. Pharm. Chim.*, 1914, [vii], 10, 100—108).—Four c.c. of blood or other liquid to be analysed, 2 c.c. of water, and 5 c.c. of sodium hypobromite solution are introduced successively into a small, graduated tube provided with a tap at each end, and filled previously with mercury. The lower part of the tube, below the graduated portion, is slightly enlarged. After the contents of the tube have been well shaken, the apparatus is immersed in water at a definite temperature, and the volume of the gas is then observed, the mercury level having been adjusted. The author finds that mercury does not liberate any gas from sodium hypobromite in the absence of urea. It is recommended that the hypobromite solution be submitted to a low pressure before use, in order to remove dissolved oxygen.

W. P. S.

Gravimetric Estimation of Urea in Blood. R. FOSSE, A. ROBYN, and F. FRANÇOIS (*Compt. rend.*, 1914, 159, 367—369. Compare Hugounenq and Morel (*Compt. rend. Soc. Biol.*, 1913, 1914).—Ten c.c. of the blood serum are mixed with 10 c.c. of Tanret's solution of potassium mercuriodide in acetic acid and centrifuged. The clear liquid measures about 17 c.c., and of this an aliquot portion, 15 c.c., is taken; to it is added 30 c.c. of glacial acetic acid and three portions of 0.75 c.c. of a 10% solution of xanthhydrol in methyl alcohol. After one hour the precipitate is collected, dried, and weighed. The urea present is equal to one-seventh of the weight of the precipitate, and the volume of defecated serum may be taken as equivalent to one-half its volume of fresh serum for purposes of calculation.

W. G.

Estimation of Caffeine in Coffee. G. FENDLER and W. STÜBER (*Zeitsch. Nahr. Genussm.*, 1914, 28, 9—20).—Although the methods described by Lendrich and Nottbohm (A., 1909, ii, 449), and by Katz (A., 1903, ii, 250), are trustworthy, they are somewhat tedious, and the following process is therefore recommended; the results obtained agree with those yields by the methods mentioned above. Ten grams of the powdered sample are shaken for thirty minutes with 10 grams of 10% ammonia and 200 grams of chloroform; the solution is then poured on a large filter, and 150 grams

of the filtrate are evaporated to dryness. The residue is digested for ten minutes with 80 c.c. of hot water, cooled, and 20 c.c. of 1% potassium permanganate solution are added (10 c.c. are sufficient in the case of raw coffee). After fifteen minutes a slight excess of hydrogen peroxide (3% hydrogen peroxide containing 1% of glacial acetic acid) is added, the mixture is heated for fifteen minutes on a water-bath, more hydrogen peroxide is added until the solution becomes clear, and then cooled and filtered, the filter and its contents being washed with cold water. The filtrate is shaken first with 50 c.c. of chloroform, then with three successive quantities of 25 c.c. of the solvent; the united chloroform extracts are evaporated to dryness, the residue of caffeine is dried at 100°, and weighed. A method proposed by Keller was found to be untrustworthy. W. P. S.

Characterisation of Morphine and Phenols by means of Uranium Salts. J. ALOY and CH. RABAUT (*Bull. Soc. chim.*, 1914, [iv], 15, 680—682. Compare 1903, ii, 581; 1905, ii, 616).—Morphine in the free state or in the form of its hydrochloride can be detected as follows. To a small amount of the alkaloid in a test-tube a few drops of methyl alcohol and a crystal of uranyl nitrate are added, when the liquid becomes coloured red. If the base is present as its hydrochloride, uranyl acetate is used instead of the nitrate, and on evaporating the liquid to dryness a red residue is left. The test will show the presence of 0.1 mg. of the alkaloid. Phenols give a similar reaction, and where they are soluble in water the alcohol can be omitted and water used in its place. The greater the number of hydroxyl groups present, the more intense is the red coloration. The presence of other groups does not, as a rule, interfere with the test, except in the case of sulphonic or nitro-groups. The colouring matter is soluble in water, and is not extracted from aqueous solution by organic solvents. It is destroyed both by acids and bases.

A red liquid is also obtained by warming uranium oxide with an aqueous solution of resorcinol, or with a solution of morphine in methyl alcohol, and from the latter solution addition of ether causes a voluminous precipitate containing uranium. W. G.

Estimation of Morphine in Pills, Tablets, Etc. J. B. WILLIAMS (*Amer. J. Pharm.*, 1914, 86, 308—312).—A number of pills or tablets, equivalent to from 0.1 to 0.2 gram of morphine, are dissolved in a few c.c. of dilute acid, the solution is transferred to a separator, 25 c.c. of a solvent consisting of 1 volume of alcohol and 2 volumes of chloroform are added, the mixture is rendered distinctly alkaline with ammonia, and shaken for three minutes. The chloroform layer is drawn off, and the extraction twice repeated with the alcohol-chloroform solvent. The extracts are evaporated to dryness, the residue dissolved in a definite quantity of *N*/10-acid, and the excess of acid is titrated with *N*/50-alkali solution, using cochineal as indicator. Each c.c. of *N*/10-acid is equivalent to 0.0301 gram of morphine. W. P. S.

Estimation of Strychnine in the Presence of Brucine. D. B. Dorr (*Pharm. J.*, 1914, 93, 120).—In the method of estimating strychnine in the presence of brucine by destroying the latter with dilute nitric acid, and then extracting the strychnine with an immiscible solvent, the best results are obtained when 1 c.c. of concentrated nitric acid is added to every 20 c.c. of the sulphuric acid solution of the two alkaloids; the action of the nitric acid should proceed for twenty minutes at the ordinary temperature. Under these conditions, 1 c.c. of nitric acid will destroy 0.25 gram of brucine without having any effect on the strychnine.

W. P. S.

Diascopy of Traces of Blood. ANGELO DE DOMINICIS (*Boll. Chim. Farm.*, 1914, 53, 162—163).—The following procedure serves to detect traces of blood in cases where all other methods fail, and is especially valuable where a very small quantity of blood is present on heavily rusted iron.

With dried blood adhering to a substrate, a scarcely visible particle is introduced into a trace of origanum oil on a microscope slide placed on a white background, and is thoroughly disintegrated by means of the rounded end of a glass rod. After the addition of a drop of a saturated or more dilute solution of eosin in paracetaldehyde, the preparation is examined in artificial light passing through a suitable diaphragm. A drop of euparal may be employed subsequently to render the preparation permanent. Where the blood has penetrated the substrate, the latter and the blood are scraped off by means of a sharp knife in the form of a fine powder, which is treated as above. Particles of blood appear wholly or partly coloured, and the red corpuscles, in groups or isolated, may be distinguished; the diameter of the corpuscles can be measured.

T. H. P.

The Analysis of Meat Extract. J. SMORODINZEV (*Zeitsch. physiol. Chem.*, 1914, 92, 214—220. Compare A., 1913, i, 1132).—The author compares four different methods for the quantitative separation of the bases from the same extract of beef: (1) precipitation of the bases with mercuric sulphate without previous treatment with lead acetate, the precipitate being then decomposed by hydrogen sulphide, and the bases isolated by means of phosphotungstic acid; (2) precipitation with phosphotungstic acid after preliminary treatment with lead acetate; (3) precipitation with phosphotungstic acid in the presence of 5% sulphuric acid; (4) direct precipitation with phosphotungstic acid without any preliminary treatment.

Expressing the results in percentages of fresh ox muscle, the first method furnished the largest amount of purine (0.062), carnosine (0.318), and carnitine (0.037), but only 0.048% of methylguanidine, as against 0.066% obtained by methods (2) or (3). The preliminary treatment with lead acetate is quite superfluous, and, indeed, leads to twice the quantity of expensive phosphotungstic acid being subsequently required, on account of the

Exhibiting action of acetates on the precipitation of the phosphogates. Method (1) is therefore recommended from all points of view.

H. W. B.

Estimation of the Acidity of Leather. PAUL NICOLARDOT (*Ann. Chim. anal.*, 1914, 19, 250—259).—The leather is extracted with chloroform to remove fatty substances, and is then boiled with water, for three hours; the acidity of the filtered solution is estimated by titration, litmus paper being the indicator. Sulphuric acid and soluble sulphates are estimated in the solution in the usual way. Another portion of the leather may be boiled with the same volume of water and for the same length of time but in the presence of barium carbonate, and the acidity of the solution is estimated after filtration. In this case, the sulphuric acid and sulphates present are converted into barium sulphate. The total sulphur is best estimated by burning the leather in a bomb apparatus with oxygen under a pressure of 10 atmospheres.

W. P. S.

Analysis of Stabilised Cocoa. L. REUTTER (*Chem. Zentr.*, 1914, ii, 169—170; from *Schweiz. Apoth. Zeit.*, 1914, 52, 308—312, 322—325, 335—339).—The usual method of submitting cocoa pods to fermentation in order to effect the ready removal of the husks has the disadvantage that the fermentation considerably affects the beans. The same object may be attained by immersing the pods for ten minutes in 1% sodium carbonate solution at 45°; the beans are then submitted to a sterilising process. Cocoa prepared in this way is known as stabilised cocoa; it does not contain pre-formed sugars or free theobromine. Caffeine is not present, but traces of essential oils can be detected. The following substances were separated from the methyl alcohol extract of the fat-free cocoa: cocoa red, $C_{40}H_{60}O_{27}N$; cocoa brown, $C_{76}H_{78}O_{34}N$; and cacaorin, $C_{10}H_{20}O_8N_8$. The theobromine is present in the cocoa in combination with other substances, and is set free when the cocoa is subjected to the action of ferments.

W. P. S.

Estimation of Certain Soluble Constituents of Soils. A. HUTIN (*Ann. Chim. anal.*, 1914, 19, 259—263).—The water soluble substances are estimated by shaking 1 kilo. of the soil with 1 litre of water for thirty minutes, and filtering the mixture after twenty-four hours' contact. The filter should be partly filled with dried paper pulp. Two hundred and fifty c.c. of the filtrate are evaporated to dryness, and the residue is weighed. This residue is then incinerated, and the ash weighed to obtain the quantity of soluble mineral matter. The alkalinity of the soil is ascertained by titrating a definite volume of the filtrate, and the chlorides are estimated by the Charpentier-Volhard method.

W. P. S.

